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Vibrational properties and matrix photochemistry of trimethyldioxorhenium(VII), $(CH_3)_3ReO_2$ †

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Gaseous, liquid and matrix-isolated trimethyldioxorhenium(VII), **1**, has been characterised (i) by the vibrational spectra of the three isotopomers, $(CH_3)_3ReO_2$, **1**-h_9, $(CD_3)_3ReO_2$, **1**-d_9, and $(CHD_2)_3ReO_2$, **1**-d_6, recorded between 4000 and 400 cm^{-1}, and (ii) by density functional theory (DFT) calculations. The spectra have been analysed with particular reference to the ν(CH) modes, whence it appears that the three methyl groups all have the same asymmetric geometry with one weak and two strong C–H bonds irrespective of the sites they occupy in the distorted C_3ReO_2 trigonal bipyramid. IR spectroscopic measurements have been used to chart the reactions activated by irradiating **1**-h_9, **1**-d_9, or **1**-d_6 isolated in a solid argon matrix with broad-band UV-visible light ($200 \le \lambda \le 800$ nm). The primary change is thus shown to involve the elimination of methane to afford the novel methylidene-rhenium(VII) compound $H_2C{=}Re(CH_3)O_2$, **2**, but a secondary change becomes evident on continued photolysis, probably resulting in the formation of the bis(methylidene) derivative $(H_2C)_2Re(O)OH$, **3**. The results are discussed in relation to the photochemistries of other alkyloxorhenium compounds.

Methyltrioxorhenium(VII), CH_3ReO_3, is now well known,[1] particularly as an efficient catalyst in a wide range of organic reactions.[2,3] Less well known is the only other methyloxorhenium(VII) compound to be isolated, namely trimethyldioxorhenium, $(CH_3)_3ReO_2$, **1**. An oil at room temperature, **1** was first synthesised by Mertis and Wilkinson by oxidation of tetramethyloxorhenium(VI) with NO.[4] Analogous compounds are rare but include R_3ReO_2, where R = CH_2CMe_3 or CH_2SiMe_3,[5a] and $R'(Me_3CCH_2)_2ReO_2$, where R′ = CH_3, CH_2SiMe_3 or Ph.[5b] Little has been made of the chemical properties of **1**, although studies of several organic reactions indicate that significant catalytic potential exists.[6]

On the evidence of the IR and ^{1}H NMR spectra, Mertis and Wilkinson concluded that the molecule of **1** has a trigonal bipyramidal (TBP) skeleton with one oxygen atom located in an axial and the other in an equatorial site.[4] More recently, however, it has been shown by a detailed study[7] of the ^{1}H, ^{13}C and ^{17}O NMR spectra of solutions, of the vibrational spectra, and of the electron diffraction pattern of the vapour that the molecular framework is a severely distorted trigonal bipyramid, perhaps better described as an edge-bridged tetrahedron (EBT), in which the oxygen atoms occupy equivalent *pseudo-equatorial* positions. Measuring 2.122 Å, the pseudo-axial Re–C bonds are slightly shorter than the pseudo-equatorial one (2.199 Å), in good agreement with the optimum dimensions deduced by density functional theory (DFT) calculations. The catalytic activity of the compound raises questions about possible oxygen atom-transfer reactions and also about its decomposition under thermal or photolytic stimuli. In the case of CH_3ReO_3, for example, very recent studies[8] have revealed that UV photolysis of the matrix-isolated molecule brings about tautomerisation with the formation of the methylidene derivative $H_2C{=}Re(O)_2OH$, an intermediate likely to be relevant, for example, to the catalysis of olefin metathesis.

Here we report the results of a detailed study of the IR and Raman spectra of different isotopic versions of **1** in the gaseous, liquid and matrix-isolated states. These are analysed in the light of DFT calculations and of the "isolated" C–H stretching frequencies ν^{is}(CH),[9] displayed by $(CHD_2)_3ReO_2$, **1**-d_6, to assess the properties of the methyl groups. In addition, we report on the matrix photochemistry of **1** by reference to the IR spectrum of the molecule isolated in a solid argon matrix at low temperatures. Hence it will be shown that the primary event on broad-band UV-visible irradiation ($200 \le \lambda \le 800$ nm) is not tautomerisation (as in the case of CH_3ReO_3)[8] but elimination of CH_4 and formation of the novel methylidene-rhenium(VII) compound $H_2C{=}Re(CH_3)O_2$, **2**. Continued photolysis gives rise to a secondary change leading probably to the bis(methylidene) product $(H_2C)_2Re(O)OH$, **3**. The identification of the products on the basis of their IR spectra has been endorsed (i) by the response to deuteriation of the precusor **1**; (ii) by comparison of the wavenumbers and intensities in IR absorption with those deduced by DFT calculations, and (iii) by analogies with the spectra of related methylidene and oxorhenium derivatives, *e.g.* MCH_2 (M = Cr, Mn, Fe, Co, Ni or Cu),[10] $H_2C{=}Re(O)_2OH$,[8] and $H_2C{=}Re(CH_3)_2O$.[11] The behaviour of **1** is compared with that of CH_3ReO_3 and other alkyloxorhenium compounds under similar conditions.

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† Electronic supplementary information (ESI) available: further details concerning the vibrational calculations and cartesion coordinates of the optimised geometries. See http://www.rsc.org/suppdata/dt/b2/b204238j/

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Experimental

Synthesis

All experiments were carried out using standard Schlenk, inert atmosphere, or high-vacuum techniques. Isotopically natural or enriched samples of hexamethyltrioxodirhenium(VI)[12] and dimethylzinc[13] were prepared according to literature methods. Perdeuteriated iodomethane was prepared by the reaction of methanol-d_4 (ex Eurisotop) with PI_3 produced *in situ*,[14] whereas the partially deuteriated compound CHD_2I was prepared from $CHBr_2Cl$ (ex Aldrich), with $Bu^n{}_3SnD$ (also produced *in situ* from $Bu^n{}_3SnCl$ and $LiAlD_4$) giving first CHD_2Cl, which was then treated with NaI in cyclohexanone solution.[15] Other chemicals were used as purchased from commercial sources. Solvents were dried by literature methods. Dirhenium heptoxide and trimethylamine-*N*-oxide (both ex Aldrich) were purified by sublimation immediately prior to use.

Trimethyldioxorhenium(VII) was synthesised as described previously[7,16] by the reaction of the anhydrous trimethylamine-*N*-oxide with hexamethyltrioxodirhenium(VI) in ether solution. After removal of the solvent *in vacuo* and washing with water to remove unchanged trimethylamine-*N*-oxide, the product was purified by trap-to-trap fractionation *in vacuo*, and its identity and purity were checked by reference to the IR spectrum of the vapour and the ^1H NMR spectrum of a CD_2Cl_2 solution.[7] Samples of the perdeuteriated compound $(CD_3)_3ReO_2$, **1**-d_9, and partially deuteriated compound $(CHD_2)_3ReO_2$, **1**-d_6, were synthesised in a similar manner from $(CD_3)_6Re_2O_3$ and $(CHD_2)_6Re_2O_3$, respectively.

Spectroscopic and matrix-isolation studies

IR spectra in the range of 4000–400 cm^{-1} were recorded for gaseous and matrix-isolated samples of **1** in its different isotopic forms using either a Mattson 'Galaxy' 6020 or a Nicolet 'Magna' 560 FT-IR spectrometer. Measurements were made at a resolution of 1 or 0.5 cm^{-1} and with a wavenumber accuracy of ± 0.1 cm^{-1}. The vapour over samples of **1**-h_9, **1**-d_9, or **1**-d_6 at room temperature was sampled in a Pyrex-bodied cell fitted with CsI windows held in place with halocarbon wax and giving a pathlength of *ca.* 20 cm. Raman spectra were recorded for liquid samples at room temperature with a Dilor Olympus BX40 spectrometer (at Imperial College London) at a resolution of 4 cm^{-1}.

For matrix-isolation experiments the vapour over a sample of **1** held at 253 K was codeposited continuously with an excess of argon on a CsI window cooled to *ca.* 12 K by means of a Displex closed-cycle refrigerator (Air Products CS 202); fuller details of the apparatus are given elsewhere.[17] Typical deposition rates were 2–3 mmol h^{-1}, continued over a period of 2 h, and the matrix ratios Ar : **1** were estimated to be *ca.* 1000 : 1. Following deposition and IR analysis of the resulting matrix, the sample was exposed to broad-band UV-visible radiation ($200 \le \lambda \le 800$ nm) for periods of 2 h or more. The photolysis source was a Spectral Energy Hg-Xe arc lamp operating at 800 W and the output from which was invariably limited by a water filter to absorb IR radiation and so minimise any heating effects.

Quantum chemical calculations

Calculations were carried out using the ADF 2000 program suite.[18,19] The electronic configuration of the $(CH_3)_3ReO_2$ molecule was described by an uncontracted triple-ζ basis set of Slater-type orbitals (STO), carbon and oxygen being given extra (3d) polarisation functions. The cores of the atoms were frozen, C and O up to 1s, Re up to 4d, and relativistic corrections were made to the cores of all atoms using the ZORA formalism. Energies were calculated using Vosko, Wilk and Nusair's local exchange correlation potential,[20] with non-local exchange corrections by Becke,[21] and non-local correlation corrections by Perdew,[22] while vibrational wavenumbers were computed by numerical differentiation of slightly displaced geometries.[23] The different degrees of anharmonicity displayed by the individual vibrational fundamentals make it unrealistic to attempt any scaling on the basis of a single scaling factor. Accordingly, the vibrational wavenumbers calculated for the molecules **1**–**3** and cited hereafter remain *unscaled.* For each of the molecules studied, further details concerning the vibrational calculations, along with the cartesian coordinates of the optimised geometry, are available as ESI.

Results and discussion

Vibrational spectra of 1-h_9, 1-d_9, and 1-d_6

Tables 1 and 2 list details (i) of the IR spectra displayed by $(CH_3)_3ReO_2$, **1**-h_9, and $(CD_3)_3ReO_2$, **1**-d_9, in the vapour and matrix-isolated states, (ii) of the IR spectra calculated for the molecules each in its optimum equilibrium geometry, and (iii) of the Raman spectra of the liquids. Representative spectra are illustrated in Figs. 1 and 2. Table 3 gives additional information concerning the ν(CH) region of the IR and Raman spectra of $(CHD_2)_3ReO_2$, **1**-d_6. In a preliminary account of some of these results,[7] consideration has already been given to the evidence they might provide about the geometry of the C_3ReO_2 skeleton, and about any secondary interactions involving the methyl and/or oxo ligands. Here we present additional information, most notably relating to the partially deuteriated isotopomer **1**-d_6, and discuss the assignment and significance of the spectra, primarily for what they reveal about the characters of the methyl groups. For this analysis we depend on the evidence (a) of the effects of complete or partial deuteriation of the methyl groups, (b) of the vibrational properties calculated for the different isotopomers of **1** by DFT methods, and (c) of analogies with

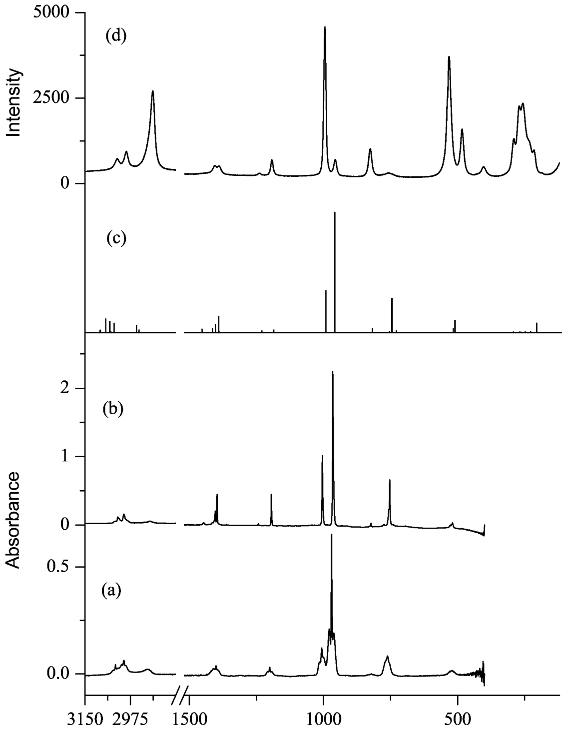


Fig. 1 Vibrational spectra of $(CH_3)_3ReO_2$, **1**-h_9: (a) IR spectrum of a gas-phase sample, (b) IR spectrum of the molecule isolated in an argon matrix at *ca.* 12 K, (c) calculated IR spectrum, and (d) Raman spectrum of the liquid.

Table 1 IR and Raman spectra of $(CH_3)_3ReO_2$, **1**-h_9, in the vapour, matrix-isolated and liquid states compared with the spectra calculated for the free molecule by DFT methods[a]

IR			Raman	
Vapour (obs.)	Ar matrix (obs.)	Calc.[b]	Liquid (obs.)	Approx. description
	3037.0 vw	3091.5 (3)		$\nu_{as}(CH_3)$
		3090.2 (0.01)	3025.2 mw	
3032.5 w	3032.5 vw	3069.8 (16)		
	3023.0 mw	3054.3 (13)	2991 m	
	3018.0 sh	3050.1 (0.8)		
3000.2 mw	3000.2 mw	3037.5 (11)		
	2920.5 vw	2951.4 (8)		$\nu_s(CH_3)$
2908.7 w	2900.2 w	2943.0 (1)	2889.5 s	
		2941.6 (3)		
	2773.4 vw		2764.7 w	$2 \times \delta_{as}(CH_3)$
	1446.0 vw	1452.8 (4)		$\delta_{as}(CH_3)$
	1414.1 vw	1412.6 (5)	1405.9 mw	
	1406.8 vw	1403.4 (0.06)		
1400.7 mw	1403.7 w	1402.2 (9)	1389.6 mw	
	1396.7 m	1390.3 (19)		
	1391.7 vvw	1386.9 (0.5)		
	1242.9 vw	1229.4 (2)	1239.1 w	$\delta_s(CH_3)$
1200.0 mw	1194.2 m	1185.3 (3)	1192.6 m	
		1181.8 (0.4)		
1007.0 m	1004.3 s	990.2 (49)	993.9 vs	$\nu_s(ReO_2)$
970.2 vs	965.7 vs	957.7 (141)	956.3 m	$\nu_{as}(ReO_2)$
		876.9 (0.06)	825.1 ms	$\rho(CH_3)$
821.8 w	822.9 vw	817.9 (5)		
	774.4 vw	760.6 (0.3)	756.6 w	
	756.1 sh	753.2 (1)		
760.9 m	752.6 m	744.2 (40)	752 w, sh	
	740.5 vw	728.3 (2)		
	527.0 w	516.0 (5)	531.7 vs	$\nu_{as}Re(C_{ax})_2$,
520.3 mw	518.9 w	509.5 (14)	482.6 s	$\nu_s[Re(C_{ax})_2 + ReC_{eq}]$,
[d]	[d]	468.2 (0.4)		$\nu_s[Re(C_{ax})_2 - ReC_{eq}]$[c]
[d]	[d]	388.5 (0.1)	402.3 mw	$\delta(C_3ReO_2) + CH_3$ torsion
[d]	[d]	291.4 (0.7)		
[d]	[d]	269.8 (0.6)	290.4 sh	
[d]	[d]	263.8 (0.8)	269.4 s	
[d]	[d]	247.6 (0.9)		
[d]	[d]	239.0 (0.2)	256.1 s	
[d]	[d]	227.0 (1.5)	232.5 sh	
[d]	[d]	205.0 (11)		
[d]	[d]	113.1 (0.2)	214.6 sh	
[d]	[d]	80.0 (1)		

[a] Wavenumbers in cm^{-1}. Intensities of observed bands: s strong, m medium, w weak, v very, sh shoulder. [b] IR intensities given in parentheses in km mol^{-1}. [c] See text. [d] Region inaccessible to present measurements.

the spectra of other methyloxorhenium and oxorhenium compounds, *e.g.* CH_3ReO_3,[8,24] $(CH_3)_4ReO$,[11] and ReO_2F_3.[25]

Structure optimisation by DFT calculations and least-squares refinement of gas electron diffraction (GED) data identify C_s as the symmetry group of the $(CH_3)_3ReO_2$ molecule in its equilibrium ground state, with both oxo ligands and one CH_3 group located in the equatorial plane of a distorted trigonal bipyramid (see Fig. 3).[7] The unique plane of symmetry contains the ReO_2 unit and a C–H bond of the pseudo-equatorial (eq) CH_3 group, while the pseudo-axial (ax) CH_3 groups are each staggered with respect to the $CReO_2$ equatorial fragment and therefore eclipsed with respect to each other. With this relatively low symmetry and the 39 normal modes spanning the representations 22a′ + 17a″, the vibrational selection rules offer little help in the interpretation of the spectra. Some simplification can be achieved, however, by dividing the modes into two classes, *viz.* (i) those associated mainly with the motions of the heavy-atom C_3ReO_2 skeleton (8a′ + 4a″), and (ii) those localised mainly in the internal or torsional modes of the methyl groups (14a′ + 13a″). The two types of mode can be distinguished, partly by the wavenumber range in which they lie (internal CH_3 vibrations apart from CH_3 rocking and torsional modes occurring at wavenumbers > 1000 cm^{-1}), and partly by their response to deuteriation of the methyl groups. Moreover, the internal modes of the different methyl groups couple only weakly[26] so that several of them emerge as being degenerate, at least within the limits of experimental measurement. This lack of coupling means too that the internal modes give few clues to the overall geometry of the molecule. Rather are they of interest primarily for their ability to report on the detailed properties of the coordinated CH_3 groups themselves.[9]

Although there are no common reference points for the IR and Raman spectra measured for a given isotopomer of **1** in the vapour or matrix and liquid states, respectively, the results show a close correlation not only of intensity and wavenumber between the IR spectra of the vapour and matrix-isolated species, but also of wavenumber between these spectra and the

Table 2 IR and Raman spectra of $(\mathrm{CD_3})_3\mathrm{ReO_2}$, **1**-$d_9$, in the vapour, matrix-isolated and liquid states compared with the spectra calculated for the free molecule by DFT methods[a]

IR			Raman	
Vapour (obs.)	Ar matrix (obs.)	Calc.[b]	Liquid (obs.)	Approx. description
	2276.3 vw	2298.2 (1.5)		$\nu_{\mathrm{as}}(\mathrm{CD_3})$
2274.3 mw	2274.0 vw	2298.0 (0.01)	2269.9 mw	
	2267.5 w	2283.2 (9)		
2244.8 mw	2243.6 w	2265.6 (8)	2237.1 m	
	2239.9 sh	2261.6 (1.5)		
	2228.2 w	2250.6 (4)		
2120.0 w	2114.6 w	2123.9 (5)		$\nu_{\mathrm{s}}(\mathrm{CD_3})$
		2116.6 (0.4)	2108.8 vs	
	2097.1 vvw	2115.3 (1.5)		
			2036.7 w	2 × $\delta_{\mathrm{as}}(\mathrm{CD_3})$
	1036.6 vvw	1058.1 (1.5)		$\delta_{\mathrm{as}}(\mathrm{CD_3})$
1032.5 w	1028.8 mw	1028.5 (1.5)		
		1021.6 (0.03)	1026.7 w	
	1021.4 w	1019.8 (1)		
	1019.3 w	1013.5 (10)		
		1009.1 (0.4)		
1008.1 ms	1006.0 s	989.6 (54)	997.8 vs	$\nu_{\mathrm{s}}(\mathrm{ReO_2})$
966.7 vs	962.3 vs	953.6 (135)	941.8 ms	$\nu_{\mathrm{as}}(\mathrm{ReO_2})$
	945.3 w	938.7 (6)		$\delta_{\mathrm{s}}(\mathrm{CD_3})$
		914.4 (0.1)	916.5 m	
	926.5 w	912.3 (2)		
	655.4 vw	653.0 (0.0006)		$\rho(\mathrm{CD_3})$
	640.5 w	636.0 (3)	641.0 mw	
	584.6 vw	573.9 (0.2)		
	573.6 sh	569.9 (0.6)	576.2 mw	
576.2 m	571.4 m	565.5 (19)		
		564.1 (1)		
	479.2 sh	469.3 (4)	488.8 s	$\nu_{\mathrm{as}}\mathrm{Re(C_{ax})_2}$, $\nu_{\mathrm{s}}[\mathrm{Re(C_{ax})_2} + \mathrm{ReC_{eq}}]$, $\nu_{\mathrm{s}}[\mathrm{Re(C_{ax})_2} - \mathrm{ReC_{eq}}]$[c]
480.4 mw	477.9 mw	467.5 (16)	438.3 m	
[d]	[d]	421.0 (0.05)		
[d]	[d]	338.0 (0.5)	358.6 mw	$\delta(\mathrm{C_3ReO_2}) + \mathrm{CD_3}$ torsion
[d]	[d]	285.2 (0.2)		
[d]	[d]	235.6 (1)	286.5 m	
[d]	[d]	234.7 (0.2)	242.0 s	
[d]	[d]	205.9 (0.9)		
[d]	[d]	203.8 (11)	213.6 sh	
[d]	[d]	181.9 (0.2)	185.1 w	
[d]	[d]	178.6 (0.09)		
[d]	[d]	88.5 (0.09)	139.9 w	
[d]	[d]	67.1 (0.9)		

[a] Wavenumbers in $\mathrm{cm^{-1}}$. Intensities of observed bands: s strong, m medium, w weak, v very, sh shoulder. [b] IR intensities given in parentheses in km $\mathrm{mol^{-1}}$. [c] See text. [d] Region inaccessible to present measurements.

Table 3 ν(C–H) regions of the IR and Raman spectra of $(\mathrm{CHD_2})_3\mathrm{ReO_2}$, **1**-$d_6$, in the vapour, matrix-isolated and liquid states compared with the results of DFT calculations[a]

IR		Raman	
Vapour (obs.)	Ar matrix (obs.)	Liquid (obs.)	Calc. mean wavenumbers
3001 mw	3000 mw	2994 m	3054 ± 9
2930 mw	2910 mw[b]	2913 m	2980 ± 4

[a] Wavenumbers in $\mathrm{cm^{-1}}$. Intensities of observed bands: m medium, w weak. [b] Multiplet pattern.

corresponding Raman spectrum of the liquid. Hence there is every reason to suppose that the monomeric molecule $(\mathrm{CH_3})_3\mathrm{ReO_2}$, $(\mathrm{CD_3})_3\mathrm{ReO_2}$ or $(\mathrm{CHD_2})_3\mathrm{ReO_2}$ is common to all these states with minimal perturbation as a result of intermolecular forces.

(i) Skeletal vibrations. The two most intense absorptions in the IR spectrum of **1**, occurring near 1000 and 970 $\mathrm{cm^{-1}}$ and with wavenumbers barely affected by deuteriation, are readily identified with the fundamentals $\nu_{\mathrm{s}}(\mathrm{ReO_2})$ and $\nu_{\mathrm{as}}(\mathrm{ReO_2})$, respectively. Raman scattering at very similar wavenumbers is observed for liquid **1**; that both bands appear to be polarised [one strongly so with a depolarisation ratio ρ = *ca.* 0.04, the other only weakly with $\rho = 0.61(7)$] is consistent with a C_s molecular model in which the $\mathrm{ReO_2}$ fragment lies in the unique plane of symmetry. The wavenumbers are very close to those reported for the corresponding modes in the molecules $[\mathrm{MO_2F_3}]^{n+}$ (M = Re, n = 0; M = Os, n = 1)[25] and $\mathrm{RReO_3}$ (R = Me,[8,24] Et,[24,27] or η^5-$\mathrm{C_5Me_5}$[1]), and give no hint of significant intra- or inter-molecular interaction involving one or both of the Re=O bonds [as has been suggested in the case of the neopentyl derivative $(\mathrm{Me_3CCH_2})_3\mathrm{ReO_2}$[5a]]. The relative intensities of the two IR absorptions are also consistent with an OReO bond angle of 123(2)°

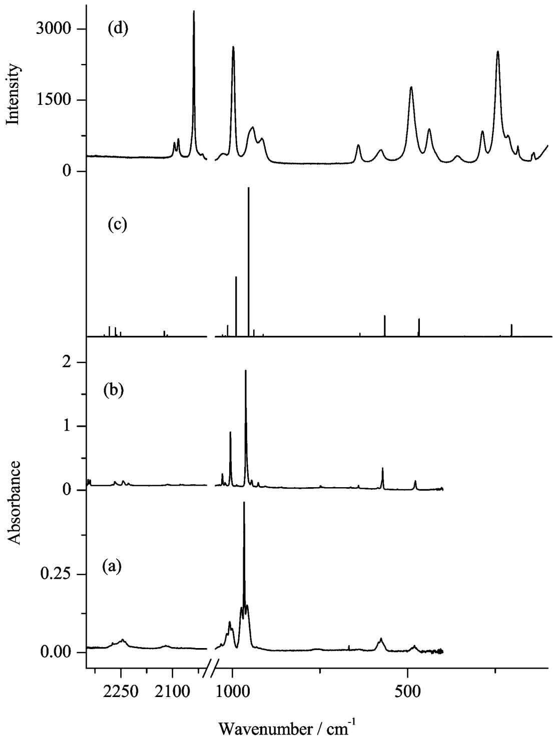


Fig. 2 Vibrational spectra of $(CD_3)_3ReO_2$, **1**-d_9: (a) IR spectrum of a gas-phase sample, (b) IR spectrum of the molecule isolated in an argon matrix at *ca.* 12 K, (c) calculated IR spectrum, and (d) Raman spectrum of the liquid.

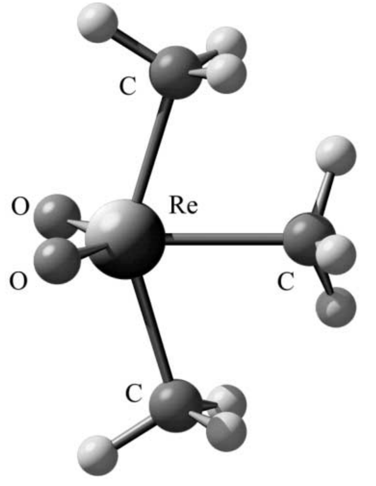


Fig. 3 The structure of $(CH_3)_3ReO_2$, **1**, in the gas phase.[7]

estimated from the electron diffraction pattern of the vapour.[7]

Much weaker IR bands near 520 and 460–480 cm^{-1}, with relatively prominent Raman counterparts, and which shift to *ca.* 480 and 430 cm^{-1}, respectively, in the spectra of **1**-d_9, are attributable to ν(ReC) fundamentals, in good agreement with the results of the DFT calculations. These calculations show that one of the three ν(ReC) modes can be described as $\nu_{as}[Re(C_{ax})_2]$, and the other two as in-phase and out-of-phase components of the coupled $\nu_{sym}[Re(C_{ax})_2 \pm ReC_{eq}]$ modes, respectively, and that the wavenumbers of the first and the second are separated by no more than a few cm^{-1}. Accordingly we are led to the assignments given in Tables 1 and 2. A similar situation is found with the three ν(MF) fundamentals of the C_{2v} species ReO_2F_3 and $[OsO_2F_3]^+$,[25] which have structures akin to that of **1** but with fluorine replacing the CH_3 groups. Skeletal deformation modes are predicted to occur with relatively low intensity in IR absorption at wavenumbers < 450 cm^{-1}. Our IR spectra did not extend to wavenumbers below about 400 cm^{-1} and did not include any features which could reasonably be ascribed to any such modes. On the other hand, the Raman spectra of the liquid samples included a number of features in the range 410–200 cm^{-1} which could plausibly be assigned, on the evidence of the calculations, to various deformation modes of the C_3ReO_2 skeleton.

(ii) Internal vibrations of the methyl groups. In the following account wavenumbers are quoted first for the molecule $(CH_3)_3ReO_2$, **1**-h_9, with the corresponding values for $(CD_3)_3$-ReO_2, **1**-d_9, being given immediately afterwards in parentheses. A manifold of C–H (C–D) stretching vibrations can be readily identified with IR and Raman features occurring at 3040–2890 (2275–2100) cm^{-1}. The IR spectrum of the vapour of **1**-h_9 shows three bands located at 3032.5, 3000.2 and 2908.7 cm^{-1} which shift to 2274.3, 2244.8 and 2120.0 cm^{-1}, respectively, in the spectrum of **1**-d_9. Such a pattern is wholly in keeping with that expected of an asymmetric methyl group having just one local plane of symmetry with two C–H bonds of one kind and one C–H bond of another kind lying in the plane. Thus, the ν_{as}(C–H) and ν_{as}(C–D) modes, which occur at higher wavenumber than the corresponding symmetric modes, each appear not as singlets but as doublets with components separated by *ca.* 30 cm^{-1}. The spectra do not appear then to discriminate between pseudo-axial and -equatorial methyl groups. Admittedly the spectra of the matrix-isolated species are more complicated, but it is impossible to decide in this case on the parts played by matrix-site effects, by the resolution of near-degenerate transitions, by the trapping of trace impurities (H_2O, CO_2, *etc.*), and/or by the trapping of more than one conformer of **1**.

CH_3 (CD_3) deformations account for two groups of bands, one appearing at 1446–1392 (1037–1019) cm^{-1} associated with δ_{as} and the other at 1243–1194 (945–927) cm^{-1} associated with δ_s modes. Rocking motions of the CH_3 (CD_3) groups are the obvious authors of bands in the region 823–741 (655–571) cm^{-1}. The wavenumbers and relative intensities are found generally to tally well with those forecast by the DFT calculations. Similar wavenumbers are also displayed by other methyloxorhenium compounds, *e.g.* CH_3ReO_3[8,24] and $(CH_3)_4ReO$.[11] Torsional modes of the CH_3 groups are predicted to occur at wavenumbers < 200 cm^{-1} and therefore below the low-energy threshold of our experimental measurements.

The observed ν(CH) wavenumbers are remarkably close to those reported for $(\eta^5\text{-}C_5H_5)Ti(CH_3)_3$, whose IR spectrum has been interpreted in terms of a modest secondary ('agostic') interaction between the metal and CH_3 groups.[28] They are comparable too with those observed[29] for the solid complex $[CH_3TiCl_3(dmpe)]$ (dmpe = $Me_2PCH_2CH_2PMe_2$), the structure of which[30] was one of the principal stimuli for the notion of an 'α-agostic' interaction.[31] On the other hand, the resemblance ends when we turn to the CH_3 deformation and rocking vibrations which consistently appear at significantly higher wavenumber than do the corresponding modes of methyltitanium compounds,[28,29,32] a feature which presumably reflects the less polar character of the Re–C bonds.

Nevertheless, the similarity of the ν(CH) wavenumbers suggests that one or more of the methyl groups in **1** resemble the methyl groups in the titanium compounds in experiencing a weakening of at least one of the C–H bonds. Such a weakening is certainly anticipated by the DFT calculations. Dimensionally the methyl groups of **1** are calculated to be virtually indistinguishable, irrespective of whether they occupy pseudo-axial or -equatorial positions. Aside from tilting about the appropriate Re–C directrix, which has been discussed previously,[7] each of the CH_3 groups is predicted to have two short C–H bonds measuring 1.0943–1.0948 Å and one long C–H bond measuring

Table 4 Isolated C–H stretching wavenumbers, ν^{is}(CH), and sum rule checks for $(CH_3)_3ReO_2$, **1**

Parameter	IR spectrum of the vapour[a]	Raman spectrum of the liquid[a]
ν^{is}(CH) (1)	3001	2994
ν^{is}(CH) (2)	2930	2913
$\Sigma\nu^{\text{is}}$(CH) [2 × 1 + 2]	8932	8901
$\Sigma\nu^{\text{is}}$(CH) [1 + 2 × 2]	8861	8820
$\Sigma\nu(CH_3)$[b]	8939	8905

[a] Wavenumbers in cm^{-1}. [b] No correction for possible Fermi resonance applied.

1.1021–1.1026 Å. The long bonds are those lying in the $Re(C_{ax})_2C_{eq}$ plane for the pseudo-axial CH_3 groups and that lying in the O_2ReC_{eq} plane for the pseudo-equatorial CH_3 group. The difference in bond length (*ca.* 0.008 Å) is too small to be detected by the GED measurements,[7] which are in any case relatively insensitive to the location of weakly scattering hydrogen atoms. Although the ν(CH) fundamentals are much more sensitive reporters on C–H bonds,[9] the information is partly coded in the spectra of the normal and wholly deuteriated molecules, partly as a result of the multiplicity of such modes and their interaction, and partly as a result of possible perturbation or even confusion created by the effects of Fermi resonance with overtones and/or combinations of $\delta_{as}(CH_3)$ or $\delta_{as}(CD_3)$ modes. It is for this reason that we have adopted the strategy developed by McKean[9] of preparing and investigating the partially deuteriated isotopomer $(CHD_2)_3ReO_2$, **1**-d_6, to access the number and wavenumbers of so-called "isolated" C–H stretching vibrations, ν^{is}(CH). With minimal coupling not only between ν^{is}(CH) modes of two or more CHD_2 groups linked to a common centre, but also between ν^{is}(CH) and other vibrational fundamentals and alleviation of the effects of Fermi resonance, the resulting wavenumbers appear to provide an unusually sensitive probe of the geometry of a CH_3 group and the strength of its C–H bonds. It should be appreciated that the timescale of the IR or Raman experiment is such that free rotation effects are not evident until the barrier to internal rotation is less than *ca.* 4 kJ mol^{-1} (100 cm^{-1}). For barriers greater than this the presence of two or three different types of C–H bond within a given methyl group may be perceived by the occurrence of two or three distinct ν^{is}(CH) bands in the spectrum of the CHD_2 derivative. Studies of other methyl-metal compounds, *e.g.* CH_3TiCl_3[32] and $(\eta^5\text{-}C_5H_5)Ti(CH_3)_3$,[28] indicate that the barriers to rotation are sufficient to satisfy this condition, and there is no reason to suppose that **1** is any exception, particularly with C_{ax}–Re–C_{eq} angles of only 74°,[7] although the non-equivalence of the CH_3 groups is a potential complication.

The asymmetric character of the methyl groups in **1** is then clearly endorsed by the observation of not one but a pair of ν^{is}(CH) bands in the IR spectrum of gaseous **1**-d_6 and also in the Raman spectrum of the liquid. These are particularly well characterised in the IR spectrum as medium-to-weak absorptions with sharp central branches located at 3001 and 2930 cm^{-1}, correlating with Raman scattering at 2994 and 2913 cm^{-1}, respectively. To determine whether this pattern arises from one strong C–H bond and two weak ones or two strong C–H bonds and one weak one, we apply the approximate sum rule for C–H stretching wavenumbers [eqn. (1)].

$$\sum_{3} \nu(\text{CH}_3) = \sum_{3} \nu^{\text{is}}(\text{CH}) \qquad (1)$$

The results listed in Table 4 indicate unequivocally the presence of two strong C–H bonds and one weak one, thereby giving pleasing affirmation of the DFT model of the molecule. No corrections for Fermi resonance have been attempted in the application of the sum rule, but the level of agreement (within 7 cm^{-1} or 0.1%) is such as to rule out Fermi resonance as having a significant influence on the measured ν(CH) wavenumbers. It is noteworthy too that the higher energy ν^{is}(CH) transition is more intense than its counterpart at lower energy, in keeping with the relative proportions of strong and weak C–H bonds, although intensities are less reliable than wavenumbers as reporters on the C–H bonds of methyl groups.

Table 5 Comparison of ν^{is}(CH) and r_0(CH) values for $(CH_3)_3ReO_2$ and other methyl-metal compounds

Molecule	ν^{is}(CH)/cm^{-1}	r_0(CH)/Å[a]	Ref.
$(CH_3)_3ReO_2$[b]	3001 × 2	1.091 × 2	This work
	2930 × 1	1.098_5 × 1	This work
$(\eta^5\text{-}C_5H_5)Ti(CH_3)_3$[c]	2943 × 1	1.098 × 1	28
	2905 × 2	1.102 × 2	28
$(\eta^5\text{-}C_5H_5)Ti(CH_3)Cl_2$[d]	2958 × 2	1.096 × 2	36
	2918 × 1	1.100 × 1	36
$(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$[d]	2932 × 2	1.098 × 2	35
	2915 × 1	1.100 × 1	35
CH_3TiCl_3[b]	2952	1.096	32
$(CH_3)_2TiCl_2$[b]	2938	1.098	32
$(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$[d]	2904	1.101	35
$(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$[d]	2900	1.102	35
$CH_3Mn(CO)_5$[b]	2955	1.096	34
$CH_3Re(CO)_5$[b]	2935	1.098	34
$(CH_3)_2Zn$[b]	2935	1.098	26
$(CH_3)_2Cd$[b]	2948	1.097	26
$(CH_3)_2Hg$[b]	2954	1.096	26
$(CH_3)_3Ga$[b]	2940	1.097	37
$(CH_3)_3Tl$[b]	2967	1.094	37
$(CH_3)_4Ge$[b]	2954	1.096	38
$(CH_3)_4Sn$[b]	2960	1.095	38
$(CH_3)_4Pb$[b]	2978	1.093	38
CH_3Cl[b]	3012	1.090	33

[a] Calculated from eqn. (2). [b] Measured for the gaseous molecule. [c] Measured for the molecule isolated in an N_2 matrix with an empirical correction to estimate the gas phase value. [d] Measured for a CCl_4 solution with an empirical correction to estimate the gas phase value.

DFT calculations on the different possible versions of the isotopomer $(CHD_2)_3ReO_2$ give wavenumbers for ν^{is}(CH) falling in two quite distinct ranges that centre on mean values of 3054 and 2980 cm^{-1} (see Table 3). Such a pattern and the separation of 74 cm^{-1} (*cf.* 71 cm^{-1} in the IR spectrum of the vapour) are in pleasing agreement with the experimental results.

McKean's empirical correlation linking r_0(CH) to ν^{is}(CH) [eqn. (2)][9] implies r_0 bond distances for the strong and weak C–H bonds of 1.0912 and 1.0985 Å, respectively.

$$r_0(\text{CH})\ (\text{Å}) = 1.3982 - 0.0001023\ \nu^{\text{is}}(\text{CH})\ (\text{cm}^{-1}) \qquad (2)$$

These compare well with the average r_e distances of 1.0945 and 1.1024 Å derived from the DFT calculations. More impressive is the difference in bond distance, namely 0.0073 Å as determined from eqn. (2) *vs.* the theoretical estimate of 0.0079 Å. Comparison of the present experimental results with those reported previously for other methyl-metal compounds (Table 5) is of interest for what it reveals about the *degree* of asymmetry of the methyl groups in **1**.

Whereas the strong C–H bonds are unusually short for a methyl-metal compound (being comparable with those in CH_3Cl[9,33]), the weak bond is similar in length to those found in $CH_3Re(CO)_5$,[34] $(CH_3)_2Zn$,[26] and the methyltitanium compounds $(\eta^5\text{-}C_5H_5)Ti(CH_3)_3$,[28] $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$,[35] and $(CH_3)_2TiCl_2$.[32] For no methyl-metal compound studied to date, however, has such a large difference in C–H bond length been encountered as that now revealed in **1**. Indeed, the weakening of one of the C–H bonds is strongly reminiscent of the behaviour of methyl groups in organic molecules such as $(CH_3)_2NH$ and $(CH_3)_2O$, where certain of the C–H bonds are significantly weakened by electronic interactions with antiperiplanar lone pairs of electrons.[9] We presume that the electronic interactions of the methyl groups with the rest of the $(CH_3)_3ReO_2$ molecule are amplified by the steric congestion created by the unusually tight C_{ax}–Re–C_{eq} bond angles[7] and by the highly unsymmetrical character of the potential energy surface defined by the torsional motions of the CH_3 groups.

A second empirical correlation noted by McKean[9] links ν^{is}(CH) with the HCH angle, *α*, of the methyl group in accordance with eqn. (3).

$$\alpha\,(°) = 0.0471\nu^{is}(\mathrm{CH})\,(\mathrm{cm}^{-1}) - 31.1 \qquad (3)$$

The unsymmetrical nature of the CH_3 groups in **1** makes it impossible to estimate more than an *average* value of *α*. However, the weighted average of the ν^{is}(CH) values implies that *α* averages to 109.1°. Another source of information is the ratio of the antisymmetric stretching wavenumbers of the CH_3 and CD_3 groups. In the approximation that the modes are 100% C–H (C–D) stretching motions and that there is no vibrational coupling between the methyl groups, this ratio is given by eqn. (4)

$$\frac{\nu_{as}(\mathrm{CH_3})}{\nu_{as}(\mathrm{CD_3})} = \left[\frac{\mu_H + \mu_C(1-\cos\alpha)}{\mu_D + \mu_C(1-\cos\alpha)}\right]^{\frac{1}{2}} \qquad (4)$$

where *μ* stands for the reciprocal of the atomic mass. Taking an average value for $\nu_{as}(CH_3)$ (3016 cm^{-1}) and $\nu_{as}(CD_3)$ (2260 cm^{-1}) and using an empirical correction factor of 1.009 to allow for anharmonicity then implies an average of 111.0° for *α*. These estimates compare well with the value of 109.6° to which we are led by the DFT calculations, with individual values ranging from 107.8 to 110.3°. Hence there is nothing to suggest that the methyl groups suffer a significant *angular* distortion.

As noted previously, each of the CH_3 groups tilts through 5–6° away from the appropriate Re–C directrix, a feature which may be due in part to bent Re–C bonds and in part to weak C–H ··· Re secondary interactions.[7] In fact, tilting seems to be the norm wherever a CH_3 group is bound to a fragment which lacks a threefold or higher axis of symmetry, *e.g.* CH_2ReO_3 in $CH_3CH_2ReO_3$[27] and CH_2X in CH_3CH_2X (where X = Cl, Br or I).[39] In that these other examples display tilt angles of only 1–2°, however, **1** stands apart in the *degree* if not the kind of distortion developed by its Re–CH_3 units.

A third correlation, also proposed by McKean,[9,40] relates ν^{is}(CH) to the C–H bond dissociation energy, $D°$(CH), by eqn. (5).

$$D°(\mathrm{CH})\,(\mathrm{kJ\,mol^{-1}}) = 0.3750\nu^{is}(\mathrm{CH})\,(\mathrm{cm}^{-1}) - 688.3 \qquad (5)$$

On this basis, $D°$(CH) for **1** is estimated to be 437 and 410 kJ mol^{-1} for the strong and weak C–H bonds, respectively. This difference of 6–7% in the C–H bond dissociation energy serves once again to emphasise the comparative insensitivity of r_0(CH) as a reporter on the strength and character of a C–H bond.

Matrix photochemistry of 1

(i) Results. The IR spectrum of an argon matrix doped with **1** in one isotopic form or another is essentially similar to that of the gaseous molecule, once due allowance is made for the potential complications of matrix site effects *etc.* and for the appearance of bands which are either masked by overlap or too weak and/or diffuse to be detected in the spectrum of the vapour. Exposure of a matrix doped with **1**-h_9 to broad-band UV-visible radiation (200 ≤ λ ≤ 800 nm) for *ca.* 15 min caused all the absorptions associated with $(CH_3)_3ReO_2$ to decay with the simultaneous appearance of new absorptions having the following wavenumbers: 3068.4, 2979.2, 2887.1, 1395.2, 1391.9, 1320.1, 1212.6, 995.6, 964.7/960.4, 830.5, 782.0, 748.6, 554.8, and 551.2 cm^{-1} (see Fig. 4). Continued photolysis under these conditions for periods of up to *ca.* 30 min led to the uniform growth of the new bands at the further expense of the bands due to the parent molecule **1**-h_9. Separate experiments involving irradiation with light spanning a narrower range of wavelengths showed that visible light (λ ≥ 400 nm) had no effect on matrix-isolated **1**, whereas UV radiation with λ = *ca.* 254 nm had the same effect as broad-band UV-visible radiation, but to a much more modest degree. Similar experiments in which matrix-isolated **1**-d_9 was subjected to broad-band UV-visible photolysis gave new IR bands at 2306.0, 2233.6, 2215.9, 2191.5, 2082.7, 1042.8, 1026.0, 1024.4, 961.3/957.4, 683.9, 664.2, 581.7, 505.3 and 501.6 cm^{-1} (see Fig. 5). In the following account, wavenumbers given in parentheses refer to the product or products in experiments with **1**-d_9.

The product bands included two of particular significance. Located at 3019.2 (2259.5) and 1303.8 (994.2) cm^{-1} (with H/D = 1.3362 : 1 and 1.3114 : 1, respectively) and both being of medium intensity, these could be identified with the formation of CH_4 (CD_4). The wavenumbers and relative intensities leave little doubt that the features correspond to the t_2 fundamentals of CH_4 (CD_4), in keeping with the IR spectra reported elsewhere[11,41] for the matrix-isolated molecule. All the other bands, which follow a common growth pattern, are then attributed to a common rhenium-containing product **2** formed by elimination of methane from **1**.

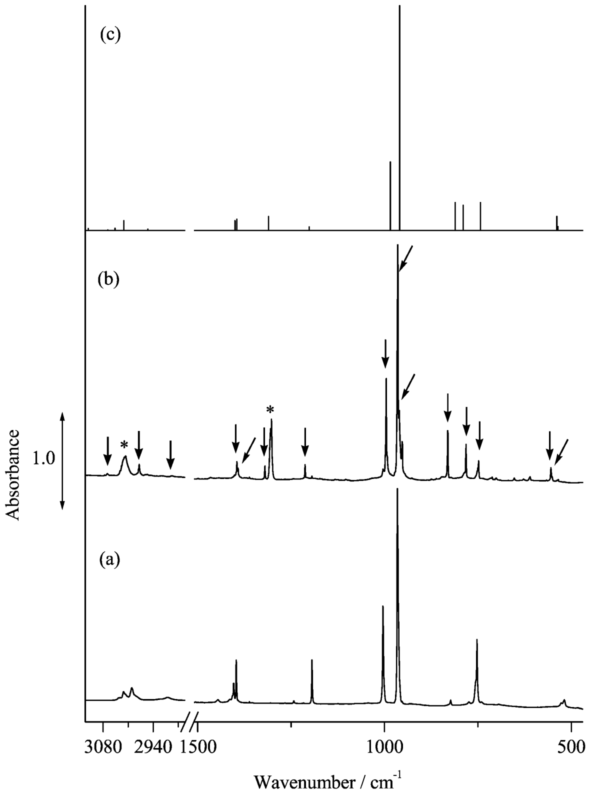


Fig. 4 IR spectrum of $(CH_3)_3ReO_2$, **1**-h_9, isolated in an Ar matrix at *ca.* 12 K (a) after deposition and (b) following broad-band photolysis (200 ≤ λ ≤ 800 nm) for a period of 165 min. (c) IR spectrum calculated for $H_2C{=}Re(CH_3)O_2$, **2**-h_5. Arrows point to bands attributable to **2**-h_5; asterisks denote bands due to CH_4.

The most prominent band of **2** occurs at 964.7/960.6 (961.3/957.4) cm^{-1} with a somewhat weaker neighbour at 995.6 cm^{-1}, the deuterio-counterpart of which is obscured by the t_2 fundamental of CD_4. The wavenumbers and relative intensities of these bands are very close to those of the two $\nu(ReO_2)$ fundamentals of **1** and so there is every reason to believe that **2**,

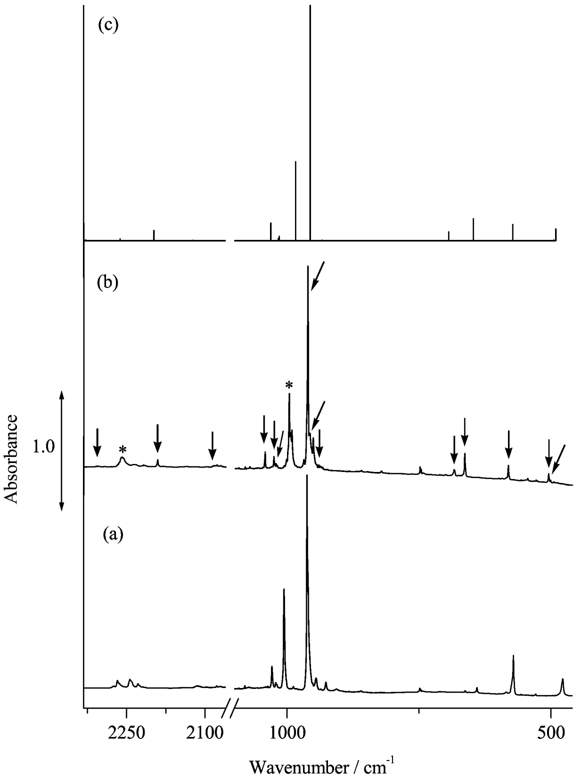


Fig. 5 IR spectrum of $(CD_3)_3ReO_2$, **1**-d_9, isolated in an Ar matrix at *ca.* 12 K (a) after deposition and (b) following broad-band photolysis ($200 \le \lambda \le 800$ nm) for a period of 105 min. (c) IR spectrum calculated for $D_2C{=}Re(CD_3)O_2$, **2**-d_5. Arrows point to bands attributable to **2**-d_5; asterisks denote bands due to CD_4.

like **1**, contains an angular ReO_2 fragment. When CH_3ReO_3 is photolysed under analogous conditions, hydrogen migration occurs from carbon to oxygen to produce the methylidene derivative $H_2C{=}Re(O)_2OH$ which is characterised *inter alia* by a strong IR absorption at 3650 (2694) cm^{-1} associated with the ν(OH) fundamental.[8] By contrast, **2** displayed no detectable absorption at wavenumbers >3068 (2306) cm^{-1}. On these grounds alone, the most obvious conclusion to be drawn is that the primary photochemical act in the case of **1** involves elimination of methane with the formation in **2** of the methylidene derivative $H_2C{=}Re(CH_3)O_2$. Fuller evidence in support of this formulation will follow in the next section.

Continued photolysis for periods of up to 250 min saw a levelling off and then decay of the bands associated with **2** and, in addition, made clear the gradual development of a distinct set of bands attributable to a second rhenium-containing photoproduct **3**. In the case of **1**-h_9, **3** absorbed at 3643.4, 3075.8, 3050.2, 952.8, 874.9, 787.1, 712.1, 701.4, 652.8, 628.1, 610.4, and 446.6 cm^{-1}; the corresponding product derived from **1**-d_9 absorbed at 2689.4, 951.5, 700.4, 599.8, 544.8, and 495.0 cm^{-1}. Among these features, that at 3643.4 (2689.4) cm^{-1} occurs in a region typically associated with ν(OH) [ν(OD)] vibrations,[8,42] while that at 952.8 (951.5) cm^{-1} lies in a region associated with ν(Re=O) vibrations.[8,11,24,25] Bands arising from **3** appeared weakly after only 10–20 minutes' photolysis but, unlike the bands due to **2**, grew steadily with progressive irradiation. The presence of only a single band near 950 cm^{-1} suggests that **3**, unlike **1** and **2**, contains just one Re=O bond, but the masking effects of absorptions due to **1** and **2** could well conceal a second absorption due to **3**.

Experiments were also carried out to determine the effects of broad-band UV-visible photolysis on matrix-isolated **1**-d_6. However, the richness of the product spectra served to complicate rather than to clarify the picture, although it was possible to identify one ν^{is}(CH) band at 3024.7 cm^{-1} attributable to the product **2**. Photolysis for periods exceeding 100 min was noteworthy only in that absorptions were observed to develop at 3643.7 and 2689.4 cm^{-1}, clearly implying the formation of different isotopic versions of **3**.

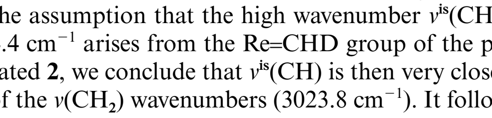
(ii) Discussion. *(a) Photoproduct* 2. The primary photoproduct formed together with methane will be shown to be the methylidene-rhenium(VII) compound $H_2C{=}Re(CH_3)O_2$ (**2**). The identification will be justified (a) by consideration of the wavenumbers and isotopic shifts of the observed IR features, (b) by reference to the vibrational properties anticipated for this molecule by DFT calculations, and (c) by analogy with the vibrational properties of known, related species.

The appearance of strong bands at 995.6 and 964.7/960.4 cm^{-1} showing minimal response to deuteriation points clearly to the presence of an ReO_2 group. A very similar wavenumber and intensity pattern is displayed, for example, by the corresponding modes of not only $(CH_3)_3ReO_2$ (**1**), but also $H_2C{=}Re(O)_2OH$[8] and ReO_2F_3.[24] The O=Re=O bond angle can be estimated roughly from the relative intensities in IR absorption of the antisymmetric and symmetric $\nu(ReO_2)$ modes, provided that these can be realistically factored out of the vibrational secular equation. A ratio I_{asym}/I_{sym} of 3.92 : 1 derived from the measured spectrum of **2** in its natural isotopic form implies that ∠O=Re=O = *ca.* 126°.

In addition, the presence of an $Re{=}CH_2$ unit in **2** is signalled by the bands at 3068.4, 2979.2, and 1320.1 cm^{-1} in the spectrum of the isotopically natural version. These shift to 2306.0, 2191.5, and 1024.4 cm^{-1} in the spectrum of the perdeuteriated form, and can be associated with the modes detailed in Table 6. Guidance is to be found here in the spectrum of $H_2C{=}Re(O)_2OH$[8] and also in those reported by Margrave *et al.* for the simple methylidene derivatives $M{=}CH_2$, where M = Cr,[10a] Mn,[10b] Fe,[10c] Co,[10d] Ni,[10e] or Cu,[10f] which have been trapped in solid argon matrices following the reaction of M atoms with diazomethane. Hence the bands of **2** at 3068.4 and 2979.2 cm^{-1} can be identified with $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$, respectively [*cf.* 3079.6 and 2985.8 cm^{-1} for $H_2C{=}Re(O)_2OH$[8]]. Confirmation of the assignment comes from the response to isotopic change with H/D = 1.3306 : 1 and 1.3594 : 1, respectively. Similarly the absorption at 1320.1 cm^{-1} (H/D = 1.2887 : 1) can be attributed to the $\delta(CH_2)$ mode of an $Re{=}CH_2$ fragment.

On the assumption that the high wavenumber ν^{is}(CH) mode at 3024.4 cm^{-1} arises from the Re=CHD group of the partially deuteriated **2**, we conclude that ν^{is}(CH) is then very close to the mean of the $\nu(CH_2)$ wavenumbers (3023.8 cm^{-1}). It follows that these C–H stretching fundamentals are little perturbed either by coupling with other modes of the molecule or by the effects of Fermi resonance. Application of eqns. (2) and (4) suggests that r_0(C–H) = 1.0888 Å and ∠HCH = *ca.* 116°, in keeping with the shorter, stronger C–H bonds and wider HCH bond angle to be expected of a CH_2 as compared with a CH_3 group.

There are therefore persuasive grounds for believing that **2** is indeed the methylidene compound $H_2C{=}Re(CH_3)O_2$ formed by elimination of CH_4 from $(CH_3)_3ReO_2$ [eqn. (5)].



$$(CH_3)_3ReO_2 \xrightarrow[\lambda = 200-800\ \text{nm}]{h\nu} H_2C{=}Re(CH_3)O_2 + CH_4 \quad (5)$$

DFT calculations find an equilibrium geometry for such a molecule conforming to C_s symmetry (see Fig. 6) with a distorted tetrahedral C_2ReO_2 skeleton and the plane of the methylidene group orthogonal to the ReO_2 fragment. The O=Re=O angle is predicted to be 122.7°, in reasonable agreement with our rough experimental estimate. Satisfactory agreement with experiment is also evident in the r_e(C–H) distance of 1.0948 Å and HCH bond angle of 115.7° delivered by the DFT calculations. The vibrational properties computed from the DFT-based force field for the isotopomers $H_2C{=}Re(CH_3)O_2$ (**2**-h_5)

Table 6 Observed and calculated IR spectra for $H_2C{=}Re(CH_3)O_2$, **2**

$H_2C{=}Re(CH_3)O_2$		$D_2C{=}Re(CD_3)O_2$		
Obs.[a, b]	Calc.[a, c]	Obs.[a, b]	Calc.[a, c]	Mode
3068.4 vw	3121.7(1.4)	2306.0 vw	2328.1 (0.5)	$\nu_{as}(CH_2)$
2979.2 w	3021.9 (7)	2191.5 mw	2197.5 (7)	$\nu_s(CH_2)$
	3067.0 (0.4)	2233.6 w	2277.8 (0.1)	$\nu_{as}(CH_3)$
	3046.6 (1.6)	2215.9 vw	2262.3 (1.2)	
2887.1 vw	2954.7 (1)	2082.7 vw	2123.1 (0.3)	$\nu_s(CH_3)$
1395.2 mw	1400.0 (7)	1042.8 m	1030.7 (12)	$\delta_{as}(CH_3)$
1391.9 w	1395.0 (8)	1026.0 m	1014.8 (3)	
1320.1 mw	1310.4 (10)	1024.4 sh	1016.6 (1.5)	$\delta(CH_2)$
1212.6 mw	1201.5 (2.5)	940.8 vw	933.4 (0.3)	$\delta_s(CH_3)$
995.6 ms	984.3 (49)		983.7 (54)	$\nu_s(ReO_2)$
964.7/960.4 s	959.4 (161)	961.3/957.4 vs	956.0 (161)	$\nu_{as}(ReO_2)$
830.5 m	811.0 (20)	683.9 mw	694.0 (6)	$\rho_w(CH_2) + \rho(CH_3) + \nu(Re{=}C)$
782.0 m	789.3 (18)	664.2 m	647.2 (15)	
748.6 mw	743.4 (20)	581.7 m	572.6 (11)	
	728.4 (0.1)		557.4 (0.04)	
	634.6 (0.003)	505.3 mw	495.4 (0.4)	$\rho(CH_2)$ + CH_2 twist + $\nu(Re–C)$
554.8 mw	538.7 (10)	501.6 w	490.9 (8)	
551.2 mw	535.6 (2.7)	[d]	395.4 (1.5)	
[d]	282.1 (1)	[d]	281.7 (1)	$\delta(C_2ReO_2)$ + CH_3 torsion
[d]	262.2 (2)	[d]	233.3 (1)	
[d]	218.7 (6)	[d]	210.5 (5)	
[d]	205.8 (3.7)	[d]	186.3 (0.3)	
[d]	204.6 (0.4)	[d]	182.7 (3.7)	
[d]	172.1 (0.06)	[d]	123.8 (0.000001)	

[a] Wavenumbers in cm^{-1}. [b] Ar matrix at *ca.* 12 K. Intensities: s strong, m medium, w weak, v very, sh shoulder. [c] DFT calculations. Intensities given in parentheses in km mol^{-1}. [d] Region inaccessible to present measurements.

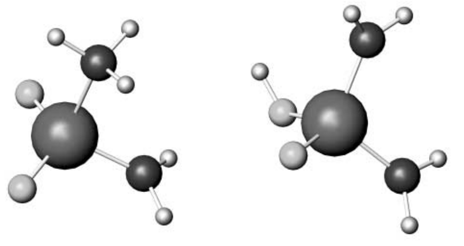
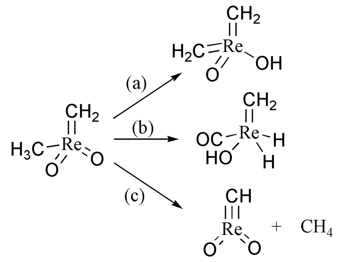

(a) (b)

Fig. 6 Structures calculated in DFT (a) for $H_2C{=}Re(CH_3)O_2$, **2**, and (b) for $(H_2C)_2Re(O)OH$, **3**.

and $D_2C{=}Re(CD_3)O_2$ (**2**-d_5) are listed alongside the corresponding experimental details in Table 6. The wavenumbers and relative intensities of the simulated spectra are thus found generally to match well the experimental results. With the guidance of the calculated properties we have succeeded in locating and assigning most of the fundamental transitions expected to appear with appreciable IR intensity in the range 4000–400 cm^{-1}. As in the case of $H_2C{=}Re(O)_2OH$,[8] there is extensive mixing of the $\nu(Re{=}C)$ and $\rho(CH_2)$ modes, and this time including also the $\rho(CH_3)$ modes, so that the region 850–750 (700–550) cm^{-1} does not lend itself to a simple interpretation based on individual group vibrations. That some fundamentals have escaped detection is perfectly understandable on the grounds of falling outside the range of the present measurements (*i.e.* < 400 cm^{-1}), being too weak to be detected, or being obscured by the absorptions of the coproduct methane or the parent compound **1**.

(b) Photoproduct 3. The results of our experiments suggest that the primary rhenium-containing photoproduct **2** is itself photolabile and undergoes a further change on prolonged irradiation with broad-band UV-visible light. The sole detectable product **3**, formed in only modest yield, could be identified by only quite a small number of transitions, most of which appeared quite weakly in IR absorption even after the longest periods of photolysis (2 h or more). At this stage virtually all signs of **1** had disappeared, and the only bands in evidence were those associated with methane, **2** and **3**. In these circumstances, the photodecomposition of **2** might be envisaged as proceeding in one of the three ways represented in eqn. (6).



(6)

Two of these, 6(a) and 6(b), involve isomerisation, the third, 6(c), elimination of a further molecule of methane to form a methylidyne derivative. The isoelectronic natures of **2** and CH_3ReO_3 suggests that **2** may well follow the example of CH_3ReO_3[8] with a tautomeric rearrangement to the bis(methylidene) hydroxo derivative $(H_2C)_2Re(O)OH$, as in 6(a). Less likely is the much more radical rearrangement to give the carbonyl compound $H_2C{=}Re(CO)(OH)H_2$ [reaction 6(b)], although a secondary product analogous to this may possibly feature in the matrix photochemistry of CH_3ReO_3.[8] The formation of the methylidyne compound $HC{\equiv}ReO_2$ may also seem somewhat implausible, particularly as it would imply extra growth of the IR absorptions due to methane. In fact, it is doubtful whether this extra growth could be detected while

Table 7 Observed and calculated IR spectra for $(H_2C)_2Re(O)OH$, **3**

$(H_2C)_2Re(O)OH$		$(D_2C)_2Re(O)OD$		
Obs.[a,b]	Calc.[a,c]	Obs.[a,b]	Calc.[a,c]	Mode
3643.4 w	3669.7 (91)	2689.4 w	2679.6 (54)	ν(O–H)
3075.8 vw	3106.0 (0.7)		2315.6 (0.3)	ν(C–H)
3050.2 vw	3098.2 (0.4)		2309.5 (0.14)	
	3005.8 (3.3)		2186.7 (3.4)	
	3002.5 (2.5)		2182.3 (4.6)	
	1313.6 (8)		1031.2 (12)	$\delta(CH_2)$
	1305.8 (6)		1024.0 (13)	
952.8 m	984.9 (108)	951.5 m	983.1 (110)	ν(Re=O)
874.9 vw	887.7 (65)	700.4 vw	696.1 (26)	$\rho(CH_2)$ + CH_2 twist + ν(Re=C) + δ(Re–OH) + ν(Re–OH) + CH_2 scissor
787.1 w	793.7 (79)		689.7 (6)	
	780.6 (13)		661.8 (68)	
712.1 w	770.1 (27)	599.8 vw	630.4 (111)	
701.4 w	738.2 (26)		610.0 (8)	
652.8 w	637.8 (105)	544.8 w	584.0 (10)	
628.1 w	626.4 (4)	495.0 vw	504.8 (2)	
610.4 w	611.7 (3)	[d]	475.0 (1.3)	
	566.3 (2.5)	[d]	423.0 (1)	CH_2 wag + δ(Re–O–H) + $\delta(C_2ReO_2)$
444.6 w	449.6 (66)	[d]	336.4 (33)	
[d]	311.8 (21)	[d]	265.8 (10)	
[d]	247.0 (5)	[d]	223.4 (2.2)	
[d]	240.8 (2.3)	[d]	211.7 (4.2)	
[d]	237.2 (1.5)	[d]	207.3 (2.3)	
[d]	210.0 (0.8)	[d]	196.4 (1.4)	
[d]	201.5 (7)	[d]	164.6 (7)	

[a] Wavenumbers in cm^{-1}. [b] Ar matrix at *ca.* 12 K. Intensities: w weak, v very. [c] DFT calculations. Intensities given in parentheses in km mol^{-1}. [d] Region inaccessible to present measurements.

methane is continuing to be released, albeit only gradually, in the primary photo-reaction 5. There is also the possibility that the product **3** is formed not from **2** but directly from **1** *via* a pathway involving, say, tautomerisation to $H_2C{=}Re(CH_3)_2(O)OH$ and competing with reaction 5. We believe this to be unlikely, however, as the absorptions characteristic of **3** continued to build up steadily even when the IR spectrum of the matrix implied that little of the precursor **1** remained. The spectroscopic evidence available to us may be limited, but we will show that it is wholly consistent with the expectation that **2** emulates CH_3ReO_3 in following the channel 6(a) to give the tautomeric product $(H_2C)_2Re(O)OH$ which is therefore to be identified with **3**.

The two most conspicuous spectroscopic markers suggest that **3** contains a single Re–OH group and at least one Re=O bond. There can be little doubt on the first point. The position and response to deuteration of the band at 3643.4 cm^{-1} (with H/D = 1.3547 : 1) are closely akin to those of the ν(OH) modes of the species $H_2C{=}Re(O)_2OH$ (3650.2 cm^{-1}, H/D = 1.3548 : 1)[8] and $HOReO_3$ (3651 cm^{-1}, H/D = 1.355 : 1).[43] Moreover, the spectrum of **3** includes no hint of a signal attributable to a ν(CO) or high-wavenumber ν(CH) mode such as might be expected for the product of reaction 6(b) or 6(c), respectively. The weight of experimental evidence leads us therefore to infer that **3** is $(H_2C)_2Re(O)OH$. Further support for this conclusion comes from the results of DFT calculations which find a potential energy minimum for such a molecule at an energy 121 kJ mol^{-1} above that corresponding to the primary photoproduct $H_2C{=}Re(CH_3)O_2$ (**2**). The structure, as illustrated and detailed in Fig. 6, again involves a pseudo-tetrahedral C_2ReO_2 heavy-atom skeleton. Table 7 compares the IR spectra measured for isotopically natural and perdeuteriated versions of **3** with those simulated for the optimum geometries of the molecules $(H_2C)_2Re(O)OH$ and $(D_2C)_2Re(O)OD$ on the basis of the DFT calculations. Despite the relative dearth of experimental information, all the observed bands attributable to **3** find a satisfactory explanation in terms of the fundamentals of one or other of these isotopomers.

(c) Mechanisms. Previous studies of the UV irradiation of solutions of CH_3ReO_3 suggest that the primary photoprocess is homolysis of the Re–CH_3 bond; under non-aqueous conditions ReO_3 is thus formed while methyl radicals abstract hydrogen atoms from the solvent to form CH_4.[44] The same primary photoprocess is presumed also to occur when the CH_3ReO_3 is confined to an argon matrix at low temperatures, but the rigid cage of argon atoms serves not only to quench any surplus energy the products may possess, but also to inhibit their escape.[8] Accordingly, recombination results, not to regenerate CH_3ReO_3 but to form the tautomeric product $H_2C{=}Re(O)_2OH$. α-Hydrogen elimination, but now through alkane-elimination [eqn. (7)],

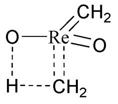
$$(Me_3CCH_2)_3ReO_2 \xrightarrow[\text{pyridine or } CH_3CN]{h\nu,\ 1\ h} Me_3C(H)C{=}Re(CH_2CMe_3)O_2 + CMe_4 \tag{7}$$

is also reported to take place when tris(isopentyl)dioxorhenium, $(Me_3CCH_2)_3ReO_2$, in a coordinating organic solvent is exposed to UV light.[5b] On the other hand, this pathway has to compete with decomposition to the dinuclear rhenium(VI) compound $(Me_3CCH_2)_2Re(O)(\mu\text{-}O)Re(O)(CH_2CMe_3)_2$ when the coordinating solvent gives way to a hydrocarbon, prompting the suggestion[5b] that the increased steric congestion created by coordination of the solvent facilitates α-hydrogen elimination.

Isolation of the parent molecule **1** in solid argon at high dilution provides its own form of steric congestion and effectively rules out any secondary reaction leading to the formation of a dinuclear product. As in the case of CH_3ReO_3, homolysis of a CH_3–Re bond through ligand-to-metal charge transfer excitation is probably the primary event, triggering the observed photochemistry of **1**. However, the initial rhenium(VI) product $(CH_3)_2ReO_2$ thereby formed differs from ReO_3 in admitting the possibility of alkane elimination *via* α-hydrogen abstraction, as opposed to H atom transfer to an Re=O unit, when confined in the same matrix cage as its $CH_3^{\bullet}$ coproduct. Although tautomerisation to give $H_2C{=}Re(CH_3)_2(O)OH$ is open to **1**, H atom abstraction to eliminate CH_4 is evidently the preferred pathway. Such behaviour is by no means unprecedented. For example, the matrix-isolated rhenium(VI) compound $(CH_3)_4ReO$ has been shown to respond to UV-visible radiation in a similar way to form CH_4 and $H_2C{=}Re(CH_3)_2O$.[11] Furthermore, Rettig *et al.* have described[45] the formation of $(P_2N_2)Ta(CH_2)CH_3$ and CH_4 by UV irradiation of $(P_2N_2)Ta(CH_3)_3$ in hexane solution at room temperature (P_2N_2 = $PhP[CH_2SiMe_2NSiMe_2CH_2]_2PPh$), and photoelimination of CH_4 also occurs from $(CH_3)_3TaX_2$ (X = 2,6-$Bu^t_2C_6H_3O$).[46]

Whether alkane elimination proceeds by two recognisably distinct steps, *i.e.* dissociation followed by abstraction, or by a more concerted mechanism involving a multicentred transition state it is hard to say, and experiments reported to date offer little guidance. On the other hand, a non-concerted mechanism offers the possibility that some of the $CH_3^{\bullet}$ radicals may escape the matrix cage and so be detectable by their IR spectrum. Close examination of the IR spectra does in fact reveal a weak absorption at 451.1 cm^{-1} following the photolysis of matrix-isolated **1**-d_9, which suggests the presence of $CD_3^{\bullet}$. The counterpart in experiments with **1**-h_9 would be obscured by the absorption at 610.4 cm^{-1} arising from photoproduct **3**. When isolated in an argon matrix, the methyl radical is reported to absorb at 617.4 ($CH_3^{\bullet}$) or 452.7 cm^{-1} ($CD_3^{\bullet}$).[47] Despite the weakness of the signal there *is* some evidence therefore that the conversion of **1** to **2** + CH_4 is indeed a two-stage process.

The methylidene derivative **2** is isoelectronic with CH_3ReO_3 and continued broad-band UV-visible photolysis might reasonably be expected to rupture the last remaining Re–CH_3 bond and so produce $CH_3^{\bullet}$ radicals and the rhenium(VI) fragment $H_2C{=}ReO_2$. The option of abstracting an α-hydrogen atom from an Re–CH_3 unit no longer existing, recombination now results not in elimination but in isomerisation with cleavage of one of the C–H bonds of the entrapped $CH_3^{\bullet}$ radical and transfer of the H atom to an oxygen atom of the ReO_2 moiety, possibly *via* the four-centre transition state **4**, to yield the observed bis(methylidene) photoproduct $(H_2C)_2Re(O)OH$ (**3**).

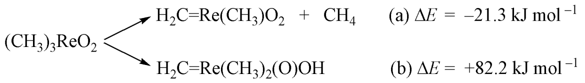


4

Conclusions

The IR and Raman spectra of three different isotopomers of trimethyldioxorhenium(VII), $(CH_3)_3ReO_2$ (**1**-h_9), $(CD_3)_3ReO_2$ (**1**-d_9), and $(CHD_2)_3ReO_2$ (**1**-d_6), have been analysed with particular reference to the properties of the methyl groups. Despite their occupancy of quite distinct sites in the distorted trigonal bipyramidal framework, the three groups are not recognisably different in their internal vibrations. Each has an asymmetric geometry with one weak and two strong C–H bonds but no significant angular distortion. The degree of asymmetry is unusually large for a methyl-metal compound, being comparable with that found in a molecule like $(CH_3)_2NH$ where weakening of C–H bonds results from interaction with an antiperiplanar lone pair of electrons.[9] This feature, together with the other dimensions and vibrational properties, is well reproduced by DFT calculations.

Isolation of **1** in a solid argon matrix at *ca.* 12 K and exposure to radiation spanning the wavelengths 200–800 nm results in α-hydrogen elimination. In the primary stage this is achieved through the elimination of CH_4, yielding the novel methylidene-rhenium(VII) compound $H_2C{=}Re(CH_3)O_2$, **2**, the properties of which have been characterised by IR measurements on the normal and deuteriated isotopomers and on the basis of DFT calculations. Such calculations confirm that CH_4 elimination [eqn. 8(a)]



$$(CH_3)_3ReO_2 \begin{cases} \rightarrow H_2C{=}Re(CH_3)O_2 + CH_4 & \text{(a) } \Delta E = -21.3 \text{ kJ mol}^{-1} \\ \rightarrow H_2C{=}Re(CH_3)_2(O)OH & \text{(b) } \Delta E = +82.2 \text{ kJ mol}^{-1} \end{cases} \quad (8)$$

is better favoured thermodynamically than is tautomerisation to form the methylidene hydroxo derivative $H_2C{=}Re(CH_3)_2(O)OH$ [eqn. 8(b), *cf.* the behaviour of CH_3ReO_3 under similar conditions[8]]. However, it is not a photodecomposition channel open to **2**, and continued broad-band UV-visible photolysis causes carbon-to-oxygen migration of a CH_3 hydrogen atom to afford the bis(methylidene) compound $(H_2C)_2Re(O)OH$, **3**, in a tautomeric change analogous to that suffered by the isoelectronic CH_3ReO_3.[8] Although detailed spectroscopic characterisation of **3** has not been possible, the combined weight of experimental and theoretical evidence would seem to leave little doubt about the identity of this product. The formation of methylidene derivatives by photodecomposition suggests that $(CH_3)_3ReO_2$, like CH_3ReO_3,[1–3] has the potential to catalyse olefin metathesis, although irreversible elimination of CH_4 must impair this function. Moreover, the properties of the trimethylrhenium compound, which is highly sensitive to attack by air and moisture and thermally fragile, make it distinctly less attractive than CH_3ReO_3 as a viable catalytic prospect.

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