Crystal Structure and High-Pressure Micro-Raman Spectra of Tricarbonyl(η^5-pentamethylcyclopentadienyl)rhenium(I), (η^5-C_5Me_5)Re$(CO)_3$

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The crystal and molecular structures of tricarbonyl(η^5-pentamethylcyclopentadienyl)rhenium(I), (η^5-C_5Me_5)Re$(CO)_3$, have been determined by single-crystal X-ray diffraction. The compound crystallizes in the triclinic space group $P\bar{1}$ (C_i^1, $Z = 2$) rather than in the $P2_1/n$ (C_{2h}^5, $Z = 4$) space group found for the (η^5-C_5H_5)Re$(CO)_3$ analog. The associated crystallographic parameters are as follows: $a = 6.9906$ (17), $b = 7.8267$ (20), $c = 12.915$ (8) Å; $\alpha = 84.91$ (4), $\beta = 87.19$ (4), $\gamma = 74.992$ (19)°; $R = 0.037$, $R_w = 0.039$. Micro-Raman spectra of crystalline (η^5-C_5Me_5)Re$(CO)_3$ have been recorded under high external pressures up to 50 kbar with the aid of a diamond-anvil cell. The discontinuities observed in the pressure vs wavenumber plots for most of the fundamentals indicate the possibility of a pressure-induced phase transition at about 9 kbar. The effect of pressure on several of these vibrational modes, especially the ν(CO) and ν(ReC) modes, is discussed in terms of the various bonding interactions involved.

Introduction

Several years ago, we initiated a broad study of the effects of high external pressures on the vibrational spectra of solid inorganic and organometallic compounds. As part of this study, we recently reported the results of a high-pressure micro-Raman investigation of (η^5-C_5H_5)Re$(CO)_3$.[1] The negative pressure dependences ($d\nu/dP$) obtained for some of the ν(CO) bands for this complex suggested that the π-back-bonding interactions between the rhenium atom and the carbonyl groups are increased by increasing external pressure, presumably due to increased charge transfer from the C_5H_5 ring to the metal. Since introduction of five methyl groups onto the C_5H_5 ring will result in substantially increased electron density on the ring and, consequently, in increased donor strength of the resulting C_5Me_5 ring compared to that of the precursor C_5H_5 ring (without effectively changing the local molecular symmetry), we felt that it would be worthwhile to perform a similar high-pressure micro-Raman study of the permethylated complex, (η^5-C_5Me_5)Re$(CO)_3$. This complex has been investigated previously by solution (^{1}H, ^{13}C, and ^{17}O) NMR,[2] gas-phase photoelectron,[3] and, most recently, IR spectroscopy.[4] The last study also included a force constant calculation.

Raman spectra in the CO stretching region of transition-metal carbonyl complexes under pressure are highly dependent on the space groups of the crystal structures concerned. For example, from a factor group analysis, the e ν(CO) mode of the C_{3v}-local-symmetry Re$(CO)_3$ moiety in (η^5-C_5H_5)Re$(CO)_3$ would be expected to split into four Raman-active components ($2a_g + 2b_g$) under C_{2h} unit cell symmetry.[5] However, only two ν(CO) peaks, together with a weak shoulder, were observed under ambient conditions. Under pressure, all four e ν(CO) factor group components appeared as a well-resolved quartet (Figure 1) as a result of the pressure-enhanced intermolecular interactions. If the crystal structure of (η^5-C_5Me_5)Re$(CO)_3$ is isomorphous with that of (η^5-C_5H_5)Re$(CO)_3$ [$P2_1/n$ (C_{2h}^5)], as is the case for (η^5-C_5Me_5)Mn$(CO)_3$ and (η^5-C_5H_5)Re$(CO)_3$,[6,7] or belongs to another monoclinic space group which has C_{2h} factor group symmetry, then similar vibrational spectra should be observed under high-pressure conditions. However, only two e ν(CO) factor group components were detected at ambient pressure and these peaks showed no peak splitting or asymmetric peak shapes for pressures up to 50 kbar (Figure 1). It seems that the (η^5-C_5Me_5)Re$(CO)_3$ and (η^5-C_5H_5)Re$(CO)_3$ complexes must have different crystal structures, and in order to clarify this situation and to obtain bonding information at ambient conditions as well as to assist in the interpretation of the high-pressure vibrational data, the X-ray crystal structure of (η^5-C_5Me_5)Re$(CO)_3$ was undertaken in the present investigation.

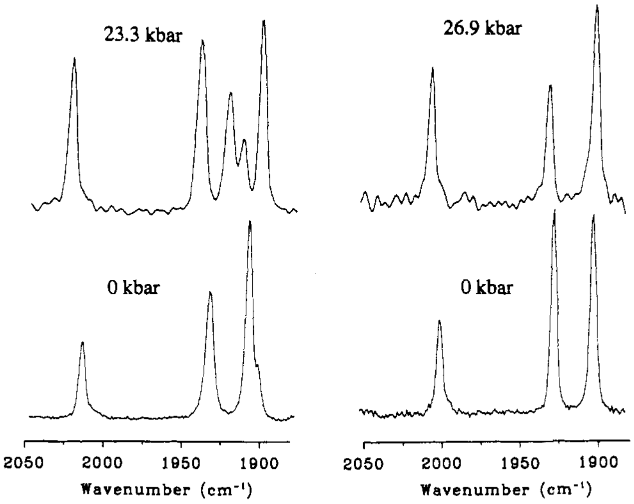

Figure 1. Comparison of the high-pressure micro-Raman spectra of (η^5-C_5H_5)Re$(CO)_3$ and (η^5-C_5Me_5)Re$(CO)_3$ (not to scale).

Experimental Section

The (η^5-C_5Me_5)Re$(CO)_3$ complex was purchased from Strem Chemicals and was purified by repeated sublimation at 90 °C/0.01 Torr immediately prior to use.

Raman Spectra. All the micro-Raman spectra were recorded on an Instruments SA U-1000 Ramanor spectrometer equipped with a Nachet

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Table I. Crystallographic Data for (η^5-C_5Me_5)Re(CO)$_3$

formula	$C_{13}H_{15}O_3Re$	Z	2
space group	$P\bar{1}$ (No. 2)	fw	405.47
a, Å	6.9906 (17)	temp, K	293 ± 1
b, Å	7.8267 (20)	μ(Mo Kα), cm^{-1}	90.6
c, Å	12.915 (8)	λ, Å	0.709 30
α, deg	84.91 (4)	ρ_{calc}, g cm^{-3}	1.982
β, deg	87.19 (4)	$R(F_o)$,[a] %	3.7
γ, deg	74.992 (19)	$R_w(F_o)$,[b] %	3.9
V, Å^3	679.6 (5)		

[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Selected Atomic Coordinates for (η^5-C_5Me_5)Re(CO)$_3$

	x	y	z	B_{eq},[a] Å^2
Re	0.99403 (5)	0.18887 (4)	0.24436 (3)	3.298 (17)
O(1)	1.1751 (13)	0.3492 (13)	0.0535 (6)	8.1 (5)
O(2)	1.3744 (12)	−0.1008 (10)	0.2862 (9)	8.9 (6)
O(3)	1.1147 (11)	0.4375 (9)	0.3834 (6)	6.1 (4)
C(1)	0.8051 (12)	−0.0075 (11)	0.2227 (8)	4.2 (4)
C(2)	0.7285 (12)	0.1510 (11)	0.1575 (6)	3.7 (4)
C(3)	0.6594 (12)	0.2926 (11)	0.2227 (8)	4.1 (4)
C(4)	0.6901 (12)	0.2230 (12)	0.3257 (7)	4.2 (4)
C(5)	0.7804 (13)	0.0388 (12)	0.3266 (7)	4.1 (4)
C(6)	0.8821 (16)	−0.1910 (13)	0.1884 (9)	6.0 (6)
C(7)	0.7111 (15)	0.1618 (15)	0.0415 (8)	5.8 (6)
C(8)	0.5474 (15)	0.4800 (12)	0.1833 (10)	6.3 (6)
C(9)	0.6258 (15)	0.3262 (17)	0.4210 (9)	6.8 (6)
C(10)	0.8178 (18)	−0.0915 (16)	0.4217 (9)	6.9 (6)
C(11)	1.1105 (14)	0.2861 (14)	0.1275 (8)	5.0 (5)
C(12)	1.2369 (15)	0.0135 (13)	0.2695 (10)	5.8 (6)
C(13)	1.0770 (12)	0.3391 (11)	0.3296 (7)	4.1 (4)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

optical microscope and interfaced to an IBM PS/2 Model 60 microcomputer. The green (514.532 nm) line of a Spectra-Physics Model 164 5-W argon ion laser was used to excite the spectra. Typical laser powers at the sample were 30 mW, and the resolution employed was 4 cm^{-1}. A 400-μm-thick, prestressed, stainless-steel gasket was located between the parallel faces of the two opposing diamonds of a diamond-anvil cell (Diacell Products, Leicester, U.K.; DAC). The sample and a small piece of ruby pressure calibrant were placed in the 400-μm hole in the center of the gasket. The purpose of the gasket was to ensure that the pressure gradient was as uniform as possible over the sample and the ruby. No pressure-transmitting fluid could be used in this particular case because the organometallic complex was soluble in all the pressure-transmitting fluids that are normally used to minimize pressure gradients. The pressure in the DAC was determined by the well-known R_1-line ruby fluorescence method.[8]

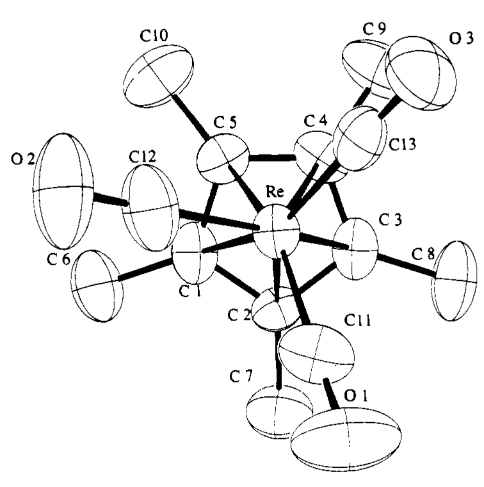

Figure 2. ORTEP projection of (η^5-C_5Me_5)Re(CO)$_3$ down the molecular axis illustrating the atomic numbering system (hydrogens are not shown).

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for (η^5-C_5Me_5)Re(CO)$_3$

Re–C(1)	2.313 (7)	C(1)–C(2)	1.432 (12)
Re–C(2)	2.311 (8)	C(1)–C(5)	1.411 (13)
Re–C(3)	2.291 (8)	C(1)–C(6)	1.496 (13)
Re–C(4)	2.286 (8)	C(2)–C(3)	1.421 (12)
Re–C(5)	2.295 (8)	C(2)–C(7)	1.502 (13)
Re–C(11)	1.875 (10)	C(3)–C(4)	1.398 (14)
Re–C(12)	1.908 (10)	C(3)–C(8)	1.528 (13)
Re–C(13)	1.891 (10)	C(4)–C(5)	1.415 (13)
O(1)–C(11)	1.162 (13)	C(4)–C(9)	1.518 (13)
O(2)–C(12)	1.145 (13)	C(5)–C(10)	1.513 (14)
O(3)–C(13)	1.169 (12)		
C(11)–Re–C(12)	90.2 (5)	C(4)–C(3)–C(8)	127.9 (9)
C(11)–Re–C(13)	90.2 (4)	C(3)–C(4)–C(5)	108.8 (8)
C(12)–Re–C(13)	89.4 (4)	C(3)–C(4)–C(9)	125.4 (9)
C(2)–C(1)–C(5)	107.3 (7)	C(5)–C(4)–C(9)	125.7 (9)
C(2)–C(1)–C(6)	126.6 (9)	C(1)–C(5)–C(4)	108.2 (8)
C(5)–C(1)–C(6)	125.9 (9)	C(1)–C(5)–C(10)	125.1 (9)
C(1)–C(2)–C(3)	107.8 (7)	C(4)–C(5)–C(10)	126.2 (9)
C(1)–C(2)–C(7)	125.7 (8)	Re–C(11)–O(1)	177.2 (9)
C(3)–C(2)–C(7)	126.3 (8)	Re–C(12)–O(2)	174.9 (9)
C(2)–C(3)–C(4)	107.9 (7)	Re–C(13)–O(3)	175.4 (7)
C(2)–C(3)–C(8)	123.8 (9)		

X-ray Crystallography. It was quite difficult to obtain a good single crystal of (η^5-C_5Me_5)Re(CO)$_3$ for X-ray structural analysis, since the complex tended to crystallize as twins in many solvents and upon sublimation. A colorless, wedge-shaped crystal with approximate dimensions of 0.33 × 0.30 × 0.25 mm, freshly recrystallized from CH_2Cl_2, was eventually used. All the measurements were performed on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα (0.7093 Å) radiation. The cell constants and the orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 24 carefully-centered reflections in the range $35.00 < 2\theta < 45.00°$, corresponded to a triclinic unit cell ($P\bar{1}$, C_i^1). The crystal and atomic coordinate data are given in Tables I and II, respectively. The intensity data were collected using the $\theta/2\theta$ scan technique to a maximum 2θ value of 54.9°. Of the 3382 reflections collected, 3128 were unique and 2576 were considered significant [$I > 2.5\sigma(I)$]. Checks after every 100 reflections showed that the intensities changed by only 0.7% throughout the data collection, and a decay correction was applied. The data were corrected for Lorentz and polarization effects. Absorption corrections were made from four ψ scans. The minimum and maximum transmission factors were 0.077 707 and 0.170 599, respectively. The hkl ranges were −8 to +9, 0 to +10, and −16 to +16, respectively. The structure was solved by direct methods (SOLVER), part of the NRCVAX system.[9] The scattering factors were taken from ref 10, and a correction was made for the secondary extinction [coefficient = 0.060 (8)].[11] The non-hydrogen atoms were refined anisotropically, and hydrogens were included in calculated positions. The final cycle of full-matrix least-squares refinement was based on 2576 observed reflections [$I > 2.5\sigma(I)$] and 155 variable parameters.

Results and Discussion

Crystal and Molecular Structure of (η^5-C_5Me_5)Re(CO)$_3$. The intramolecular bond lengths and angles associated with the non-hydrogen atoms in (η^5-C_5Me_5)Re(CO)$_3$ are listed in Table III. A projection of an isolated molecule down the molecular axis is illustrated in Figure 2. As expected, the Re(CO)$_3$ fragment possesses effective C_{3v} local symmetry, with the molecular axis passing through the midpoint of the C_5Me_5 ring and being coincident with the C_3 axis of the Re(CO)$_3$ unit. However, the overall molecular symmetry is only C_1. The plane containing the atoms Re, C(12), and O(2) is twisted 9.2° anticlockwise from that comprising atoms C(3) and Re and the midpoints of the C_5Me_5 ring and the C(5)–C(1) bond. Alternatively, the Re–C(13)–O(3) group is 5.5° in the opposite sense from being eclipsed with C(4). The corresponding values for (η^5-C_5H_5)Re(CO)$_3$ are

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Table IV. Relevant Structural Parameters for $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ and $(\eta^5\text{-}C_5H_5)Re(CO)_3$

	$(\eta^5\text{-}C_5Me_5)Re(CO)_3$	$(\eta^5\text{-}C_5H_5)Re(CO)_3$[a]
mean Re–C(O) dist, Å	1.891 (10)	1.894 (4)
mean C–O dist, Å	1.159 (13)	1.160 (1)
Re–ring dist, Å	1.959 (8)	1.957
mean Re–C–O angle, deg	175.8 (8)	177.7 (4)
mean (O)C–Re–C(O) angle, deg	89.9 (3)	90.0 (2)

[a] From ref 5.

Table V. Pressure Dependences of Observed Raman Bands of $(\eta^5\text{-}C_5Me_5)Re(CO)_3$

Low-pressure phase			High-pressure phase			
ν, cm^{-1}	dν/dP, cm^{-1} kbar^{-1}	d ln ν/d^P, kbar^{-1} × 10^2	ν, cm^{-1}	dν/dP, cm^{-1} kbar^{-1}	d ln ν/dP, kbar^{-1} × 10^2	assgnt[a]
2991	0.80	0.027	*b*			ν(CH)
2970	0.82	0.028	*c*			
2935	0.92	0.031	*b*			
2925	0.82	0.0028	*b*			
1997	0.30	0.015	*b*			ν(CO), a_1
1925	0.00	0.00	1926	0.22	0.010	ν(CO), e
1900	–0.22	–0.012	1899	0.07	0.004	
1423	0.62	0.044	*b*			ν(CC)
1034	0.15	0.015	1037	0.32	0.031	$\rho(CH_3)$
635	0.00	0.00	637	0.22	0.034	δ(Re–CO), a_1, e
			609	0.42	0.069	
591	0.86	0.15	600	0.46	0.077	
545	0.96	0.18	551	0.25	0.045	
509	0.80	0.16	516	0.11	0.021	ν(ReC), e
505	0.25	0.050	507	–0.12	–0.024	ν(ReC), a_1
381	0.41	0.11	*b*			ring tilt
109	1.76	1.61	*c*			δ(CReC), a_1

[a] From ref 4, assuming C_{3v} symmetry for the $Re(CO)_3$ moiety. [b] No break in slope at the transition pressure. [c] No points available, since the signal became too weak in this phase to measure.

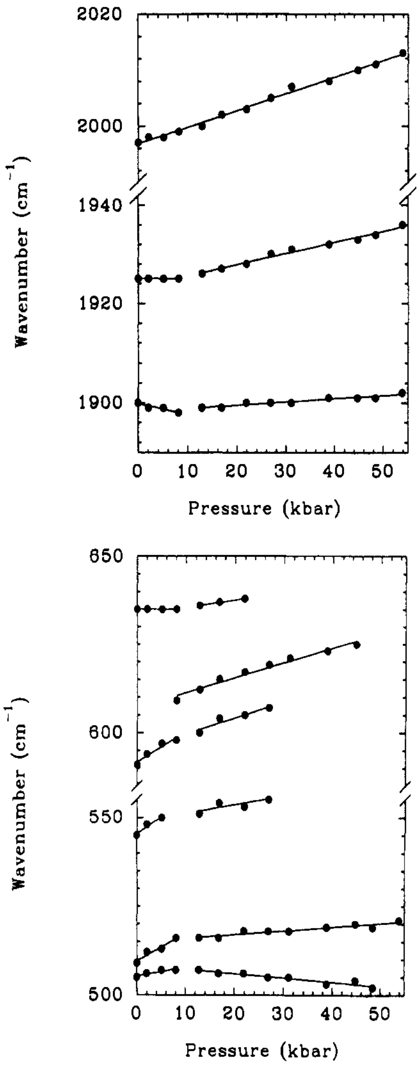

Figure 3. Pressure dependences of the Raman bands associated with the $Re(CO)_3$ moiety in $(\eta^5\text{-}C_5Me_5)Re(CO)_3$.

6.61 and 4.92°, respectively.[5] Interestingly, this structure is entirely different from that of $(\eta^5\text{-}C_5Me_5)Mn(CO)_3$, where the molecule crystallizes in the $P2_1/m$ unit cell and possesses a mirror symmetry in the lattice.[5]

The five carbon atoms of the permethylated cyclopentadienyl ring in $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ are almost planar, with the largest deviation being only 0.005 Å. The C_5Me_5 ring possesses 5-fold symmetry within experimental error. All five methyl groups are bent slightly away from the plane, and the average distance of the carbon atoms above the plane is 0.117 Å. The average C(ring)–C(methyl) bond length in $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ is 1.511 (13) Å, slightly longer than that in the $(\eta^5\text{-}C_5Me_5)Mn(CO)_3$ analog [1.465 (28) Å].[6]

Some selected structural data for $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ and $(\eta^5\text{-}C_5H_5)Re(CO)_3$ are compared in Table IV. The structural parameters for these two complexes are essentially the same, implying that the bonding situations in both compounds are quite similar. However, the differences in the CO stretching force constants for $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ (15.1 mdyn Å^{-1})[4] and $(\eta^5\text{-}C_5H_5)Re(CO)_3$ (16.0 mdyn Å^{-1}),[7] together with the measured ^{13}C- and ^{17}O-NMR chemical shifts, suggest that the π-back-bonding between the Re atom and the CO groups is stronger in $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ than it is in $(\eta^5\text{-}C_5H_5)Re(CO)_3$. It appears that both vibrational and NMR spectroscopies are more sensitive to the structural variations caused by changes in the extent of the π-back-bonding in this particular case than is X-ray diffraction.

High-Pressure Micro-Raman Spectra. The micro-Raman spectra of $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ were measured for various pressures up to about 50 kbar. The dν/dP and d ln ν/dP values for the observed Raman-active modes are given in Table V. The pressure dependences of the peaks associated with the ν(CO), ν(ReC), and δ(Re–CO) vibrations are plotted in Figure 3. Many of the observed peaks exhibit changes in pressure dependence at about 9 kbar, and most of these peaks are associated with the vibrations of the $Re(CO)_3$ moiety. These discontinuities suggest the possibility of a pressure-induced phase transition. A similar transition was detected at about the same pressure for $(\eta^5\text{-}C_5H_5)Re(CO)_3$. Because the changes in slope are gradual and the spectra in both phases are very similar, the transition is probably second order, and both phases must have very similar structures.

In the triclinic $P\bar{1}$ (C_i^1) crystal lattice, the degeneracy of the e ν(CO) mode for an isolated $Re(CO)_3$ fragment in $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ would be lifted by the C_1 site symmetry, resulting in two IR/Raman-active components (2a), and each of these modes should split further into one Raman-active (a_g) and one IR-active (a_u) mode, since the rule of mutual exclusion will apply to the centrosymmetric C_i unit cell. Therefore, no factor group splitting would be expected in either the Raman or the IR spectrum.

The pentamethylated molecule packs into a unit cell which has a lower symmetry (actually a subgroup) than does that of the parent compound, $(\eta^5\text{-}C_5H_5)Re(CO)_3$. Since the phase transition is most likely second order, the space group of the high-pressure phase should be a subgroup of the parent low-pressure structure. At the phase transition, no new vibrational peaks appear and none is lost in the internal mode region. Accordingly, it might be proposed that application of pressure probably lifts the centrosymmetric character of the low-pressure phase unit cell, resulting in a noncentrosymmetric triclinic $P1$ cell, with only one molecule per unit cell. This should lead to a change in the numbers of lattice modes but, unfortunately, this region could not be monitored under pressure due to the strong, laser-induced, fluorescence background from the diamonds.

The pressure dependences of the ν(CO) stretching modes of (η^5-C_5Me_5)Re(CO)$_3$ display behavior similar to that of the analogous modes of (η^5-C_5H_5)Re(CO)$_3$. The highest energy band, at 1997 cm^{-1}, associated with the a_1 ν(CO) vibration, shifts slowly to higher energies with increasing pressure. The pressure insensitivity of the 1925-cm^{-1} band and the negative dν/dP value for the 1900-cm^{-1} band, both of which are associated with the e ν(CO) mode, indicate that the π-back-bonding interactions between the rhenium atom and CO groups are strengthened by the application of external pressures in the low-pressure phase. Calabro and co-workers[3] have pointed out that the rhenium atom is highly effective at transferring charges from the cyclopentadienyl ring to the coordinated carbonyl ligands. If this is also true under pressure, then larger negative dν/dP values would be expected for the ν(CO) modes in (η^5-C_5Me_5)Re(CO)$_3$ than for those in (η^5-C_5H_5)Re(CO)$_3$. However, the ν(CO) pressure dependences are about the same for both complexes and the lowest energy ν(CO) band in (η^5-C_5Me_5)Re(CO)$_3$ has a even smaller negative dν/dP value than does the corresponding mode in (η^5-C_5H_5)Re(CO)$_3$. This situation is probably due to the fact that the π-acceptor ability of a carbonyl group has certain limitations. Since the π-back-bonding between the Re atom and the CO groups in (η^5-C_5Me_5)Re(CO)$_3$ is stronger at ambient pressure than is that in (η^5-C_5H_5)Re(CO), the electron density in the π^*-orbitals is already greater than that in the (η^5-C_5H_5)Re(CO)$_3$ complex. Consequently, only relatively small amounts of charge can be accommodated and this is probably why the pressure dependences of the ν(CO) modes for the two complexes are about the same.

Three of the Re–CO bending modes have relatively large dν/dP values, implying that, under pressure, the bond angles of the nonlinear Re–C–O bonds may deviate from their values at ambient conditions. Two ReC stretching modes were observed. From a comparison of their pressure dependences with those of the CO stretching vibrations, the band initially positioned at 509 cm^{-1} can be assigned as a component associated with the a_1 ν(ReC) mode and the other one, appearing at 505 cm^{-1} at ambient conditions, is the peak related to the e ν(ReC) mode. The dν/dP value of the ring tilt mode at 381 cm^{-1} is only about half that of the corresponding value for (η^5-C_5H_5)Re(CO)$_3$. The very large d ln ν/dP value obtained for the a_1 C–Re–C bending vibration at 109 cm^{-1} suggests that significant changes occur in the (O)C–Re–C(O) angles upon application of pressure.

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Supplementary Material Available: Tables of calculated hydrogen atom parameters and anisotropic thermal parameters for (η^5-C_5Me_5)Re(CO)$_3$ (1 page). Ordering information is given on any current masthead page. A table of observed and calculated structure factors may be obtained directly from the authors.