the Re–Re frequencies in the vibronic experiment (249 and 252 cm^{-1}) are lower than in the TR^3 experiment (262 cm^{-1}) because the eclipsed halides maintained by crystal constraints in the former case sterically prevent the metal atoms from assuming a metal–metal distance as short as they are permitted to in the staggered conformation allowed by the solution conditions and the time scale of the latter. The frequencies reflect these differing bond distances. Using Woodruff's rule,[20,21] we can calculate the changes in the Re–Re bond length for $^*Re_2Cl_8^{2-}$ compared to the ground state.[22] The ground-state, TR^3, and vibronic metal–metal frequencies of 274, 262, and 249 cm^{-1} yield bond distances of 2.239, 2.276, and 2.320 Å, respectively. Thus, we estimate that the relaxed, staggered (solution TR^3) excited-state metal–metal distance is 0.037 Å longer than the ground-state distance, while the eclipsed (single-crystal vibronic) excited-state distance 0.081 Å longer than that of the ground state. In our view, the eclipsed halides constrain the excited-state bond distance to be approximately 0.04 Å longer than it is in the relaxed, staggered structure.

The decrease in formal Re–Re bond order from 4 to 3 upon $\delta \rightarrow \delta^*$ excitation has the expected effect of increasing the Re–Re bond distance. A similar effect of diminished bond order is noted in the Mo dimer (Table I). In this complex, however, the excited-state Mo–Mo frequencies are the same whether measured by TR^3 spectroscopy or by vibronic methods. This fact is consistent with the $Re_2X_8^{2-}$ results in that, because the Mo dimer is sterically prevented from undergoing torsional distortion, the TR^3 and vibronic experiments probe essentially the same structure and therefore give the same excited-state Mo–Mo stretching frequency.

The vibronic and TR^3 frequencies of the $\delta\delta^*$ excited states of the two $Re_2X_8^{2-}$ complexes are summarized in Table I, along with the ground-state resonance Raman frequencies and the ground-state vibronic frequencies ($Re_2Cl_8^{2-}$ only). The systematic differences between the vibronic and TR^3 excited-state frequencies are evident not only in the Re–Re stretch but in the Re–Re–X angle bend as well. The Re–Re–X frequencies provide essentially the same information as the Re–Re stretches; indeed, these two quantities are approximately linearly related for all of the observations tabulated ($\delta(MMX)/\nu(MM) \approx 0.40$ for $Re_2Br_8^{2-}$ and 0.56 for $Re_2Cl_8^{2-}$), as expected for stretching and angle bending vibrations belonging to the same Re–Re–X structure. While the vibronic data on $Re_2Cl_8^{2-}$ suggest an eclipsed-halide (D_{4h}) excited-state structure in the crystal, the TR^3 data suggest that the relaxed structure of the excited state in solution differs from that in the crystal. The arguments presented above lead us to infer that substantial torsional distortion, probably to D_4 or D_{4d} symmetry, occurs upon excitation in solution. The quadruply bonded complexes appear to be systems in which the environment strongly influences excited-state structure and, inferentially, affects the photochemistry that the excited state may undergo. The importance of TR^3 spectroscopy in probing these excited-state structures under chemically relevant conditions is clearly demonstrated by this work.

Acknowledgment. Portions of this work were performed at Los Alamos National Laboratory under the auspices of the U.S. Department of Energy and supported by an LANL Institutional Supporting Research Grant (W.H.W.). Additional support by the National Science Foundation (Grant CHE 84-0336 at The University of Texas at Austin (W.H.W.)) and the Division of Chemical Sciences, Office of Energy Research, U.S. Department of Energy (A.P.S.) is gratefully acknowledged. We thank Dr. Stephen Atherton and the Center for Fast Kinetic Research at The University of Texas at Austin (NIH Grant RR 00886) for assistance in obtaining the transient difference spectra and Drs. David Morris and Brian Dyer for technical assistance and helpful discussions.

---

(20) Conradson, S. D.; Sattelberger, A. P.; Woodruff, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 1309.

(21) Miskowski, V. M.; Dallinger, R. F.; Christoph, G. G.; Morris, D. E.; Spies, G. H.; Woodruff, W. H. *Inorg. Chem.* **1987**, *26*, 2127.

(22) The pertinent equations are given in Table I of ref 20.

Contribution from the Department of Chemistry, McGill University,
801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6

High-Pressure Micro-Raman Study of Crystalline Tricarbonyl(η^5-cyclopentadienyl)rhenium(I), (η^5-C_5H_5)Re(CO)$_3$

Yining Huang, Ian S. Butler,* and Denis F. R. Gilson*

Received June 28, 1990

Micro-Raman spectra of crystalline CpRe(CO)$_3$ (Cp = η^5-C_5H_5) have been recorded at several different pressures up to 40 kbar. The discontinuities observed for most of the fundamentals at about 9 kbar in the slopes of the wavenumber/pressure (ν_i/P) plots suggest the occurrence of a phase transition. The pressure dependences of the CO and Re–CO stretching modes indicate that the back-bonding interactions between the Re atom and the CO groups are appreciably strengthened by increasing external pressure in the low-pressure phase, most probably due to increased charge transfer from the Cp ring to the metal. The effects of pressure on several of the fundamental modes are discussed in terms of intra- and intermolecular interactions.

Introduction

The use of pressure as an independent variable to examine the phase behavior of organometallic carbonyl compounds is of particular importance, since many of these compounds do not exhibit phase transitions on lowering the temperature but may do so when high external pressures are applied.[1-5] These pressure studies are usually performed by using diamond-anvil cells in which the samples are squeezed together between the parallel faces of two diamonds. Diamond-anvil cell Raman spectroscopy is an extremely useful technique for studying this class of compounds because the CO stretching region (ca. 2000 cm^{-1}) is free from interference from the background fluorescence arising from the diamonds. This is an important spectral region for pressure work because it has recently been shown that metal–CO interactions and the molecular geometry of metal carbonyl compounds are

---

(1) Adams, D. M.; Ekejiuba, I. O. C. *J. Chem. Phys.* **1982**, *77*, 4793.

(2) Adams, D. M.; Davey, L. M.; Hatton, P. D.; Shaw, A. C. *J. Mol. Struct.* **1982**, *79*, 415.

(3) Adams, D. M.; Hatton, P. D.; Shaw, A. C.; Tan, T. K. *J. Chem. Soc., Chem. Commun.* **1981**, 226.

(4) Adams, D. M.; Ekejiuba, I. O. C. *J. Chem. Phys.* **1983**, *78*, 5408.

(5) Huang, Y.; Butler, I. S.; Gilson, D. F. R.; Lafleur, D. *Inorg. Chem.*, in press.

0020-1669/91/1330-1098$02.50/0 © 1991 American Chemical Society

Table I. Pressure Dependences of Observed Raman Bands of $CpRe(CO)_3$

low-pressure phase			high-pressure phase			
ν, cm^{-1}	dν/dP, cm^{-1}/kbar	d ln ν/dP, kbar^{-1} × 10^{-2}	ν, cm^{-1}	dν/dP, cm^{-1}/kbar	d ln ν/dP, kbar^{-1} × 10^{-2}	assgnt[a]
3133	2.75	0.088	3158[b]	0.98[c]	0.031	ν(CH), a_1, FR[h]
3126	2.14	0.068	3146[d]	1.57[c]	0.050	2016 cm^{-1} (ν(CO), a_1) + 1107 cm^{-1} (ν(CC), a_1), FR[h]
3109	0.30	0.0096	*e*			ν(CH), e_1
3100	0.65	0.021	*e*			ν(CH), e_2
2016	0.45	0.022	2019	0.34	0.017	ν(CO), a_1
1935	0.00	0.00	1936	0.39	0.020	ν(CO), e
			1917	0.43	0.022	
1910	−0.16	−0.0080	1911	0.34	0.018	
1904	−0.45	−0.023	1901	0.045	0.0023	
1422	0.16	0.011	1424	0.23	0.016	ν(CC), e_1
1417	0.00	0.00	1418	0.18	0.012	
1107	0.61	0.055	1113	0.42	0.037	ν(CC), a_1
1063	0.47	0.044	*e*			γ(CH), e_2
1056	0.38	0.036	*e*			
933	0.97	0.10	942	0.027	0.0028	γ(CC), e_2
839	0.48	0.057	843	0.34	0.039	γ(CH), e_1
825	0.00	0.00	826	0.19	0.023	γ(CH), a_1
616	0.61	0.098	622	0.33	0.048	δ(Re–CO), a_1, e
516	1.22	0.23	526	0.35	0.066	ν(ReC), e
			514	0.55	0.11	
510	0.00	0.00	512	0.067	0.013	ν(ReC), a_1
383	0.93	0.24	394	0.68	0.17	ν(Re–Cp), e_2
349	0.74	0.21	356	0.46	0.13	ν(Re–Cp), e_1
330	0.77	0.23	338	0.49	0.14	ν(Re–Cp), a_1
129	1.73	1.34	*f*			δ[Cp–Re(CO)$_3$], e
114	1.54	1.29	127[g]	0.71	0.56	δ(CReC), e
100	1.38	1.35	*f*			δ(CReC), a_1

[a] From refs 9 and 10. [b] Fit of curve: $0.018P^2 + 0.98P + 3148 = 0$. [c] Initial slopes. [d] Fit of curve: $-0.012P^2 + 1.58P + 3132 = 0$. [e] No break in slope at transition pressure. [f] No points available since signal became too weak in this phase. [g] Only two points available in this phase. [h] Fermi resonance pairs.

extremely sensitive to the effects of pressure.[1,3–5] The complementary IR technique is not so useful because the CO stretching region is completely masked by a very strong absorption band due to the diamonds.

The structure of tricarbonyl(η^5-cyclopentadienyl)rhenium(I), $CpRe(CO)_3$ (Cp = η^5-C_5H_5), has been the subject of numerous investigations. The barrier to Cp ring rotation has been estimated from proton spin–lattice relaxation time measurements to be 7.15 kJ mol^{-1}.[6] An examination of the dipolar coupling constants in the ^{1}H NMR spectra of $CpRe(CO)_3$ in nematic liquid crsytalline solvents suggests that the Cp ring is distorted from a regular pentagon.[7] This has since been substantiated by X-ray diffraction, and the molecular symmetry of $CpRe(CO)_3$ is best described as C_s.[8] The $CpRe(CO)_3$ molecule crystallizes in the monoclinic $P2_1/n$ space group, in which the four molecules per unit cell are located at general positions. Two vibrational studies have thus far been reported. Lokshin and co-workers[9] have assigned the IR and Raman spectra on the basis of the C_{5v} and C_{3v} local symmetries of the $(C_5H_5)Re$ and $Re(CO)_3$ fragments, respectively, and by assuming that there is no interaction between the Cp ring and the $Re(CO)_3$ moiety. Chhor and Lucazeau[10] have investigated the temperature dependences of the low-frequency vibrational modes and have attributed their data to dynamic disorder. We report here the results of a high-pressure, diamond-anvil cell, micro-Raman spectroscopic investigation of crystalline $CpRe(CO)_3$ at several different pressures up to about 40 kbar.

Experimental Section

$CpRe(CO)_3$ was purchased from Strem Chemical Co. and was purified by repeated sublimation (40 °C/0.01 Torr) immediately prior to use.

Raman measurements were performed on an Instruments SA U-1000 Ramanor spectrometer equipped with a Nachet optical microscope and interfaced to an IBM PS/2 Model 60 microcomputer. The 514.532-nm (green) line of a Spectra-Physics Model 164, 5-W argon ion laser was used to excite the spectra. The power was usually about 30 mW at the sample. The resolution was typically 4 cm^{-1}. A 400 μm thick gasket was placed between the faces of the two opposing diamonds of a diamond-anvil cell (Diacell Products, Leicester, U.K., DAC). The pressure was determined by the well-known R_1-line ruby method.[11] The sample and a tiny ruby chip were placed carefully in the 400-μm hole of the stainless steel gasket. The DAC was then clamped onto an X–Y stage, and the laser beam was focused onto the sample through a 4X microscope objective. The back-scattered radiation was also collected through the same objective.

Results and Discussion

The assumption of local symmetry for the assignment of the vibrational spectra of the $CpM(CO)_3$ (M = Mn, Re) complexes has been criticized, since C_{5v} local symmetry for the $(C_5H_5)M$ moiety does not satisfactorily account for the observed vibrational data.[12,13] In this paper, we will base our assignments on those reported by Lokshin et al. because breakdowns in the local symmetry approximation result only in the e_2 species of the $Re(CO)_3$ moiety becoming IR active, while the e_1 and e_2 ring vibrations become partly polarized in the Raman spectrum.

The values for pressure dependences, dν/dP, and relative pressure dependences, d ln ν/dP, are given in Table I. Figure 1 shows typical plots of frequency versus pressure for the Raman-active modes in the CO and Re–CO stretching regions. Most of the vibrational modes show a distinct break in the slopes of the ν–P plots at about 9 kbar. These discontinuities provide evidence of a phase transformation to a new structure at this pressure. This phase transition is also indicated by the appearance of new peaks in the CO and Re–CO stretching regions (Figures 2 and 3). Since the spectra in both phases are very similar and the changes in

---

(6) Gilson, D. F. R.; Gomez, G.; Butler, I. S.; Fitzpatrick, P. J. *Can. J. Chem.* **1983**, *61*, 737.

(7) Gilson, D. F. R.; Fitzpatrick, P. J.; Butler, I. S. *Organometallics* **1984**, *3*, 387.

(8) Fitzpatrick, P. J.; Page, Y. L.; Butler, I. S. *Acta Crystallogr.* **1981**, *B37*, 1052.

(9) Lokshin, B. V.; Klemenkova, Z. S.; Makarov, Y. V. *Spectrochim. Acta* **1967**, *28A*, 2209.

(10) Chlor, K.; Lucazeau, G. *Inorg. Chem.* **1984**, *23*, 462.

(11) Piermarini, G. J.; Block, S. *Rev. Sci. Instrum.* **1975**, *46*, 973.

(12) Adams, D. M.; Squire, A. *J. Organomet. Chem.* **1973**, *63*, 381.

(13) Fitpatrick, P. J.; Page, Y. L.; Sedman, J.; Butler I. S. *Inorg. Chem.* **1981**, *20*, 2852.

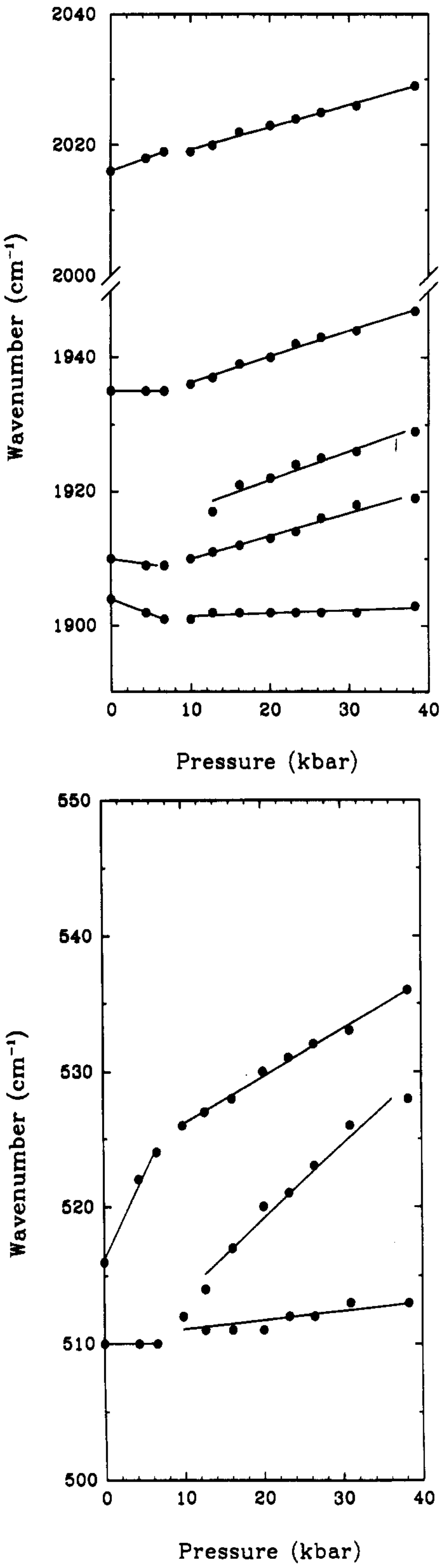

Figure 1. Pressure dependences of observed Raman bands of $CpRe(CO)_3$ in the ν(CO) and ν(ReC) regions.

pressure dependences are gradual, this transition is probably second order and the structures of both phases must be quite close.

The C–O stretching region is the most affected by the application of pressure. In addition to the three bands reported by Lokshin and co-workers, there is an obvious shoulder at ambient pressure at 1904 cm^{-1}. In the low-pressure phase, the highest energy band at 2016 cm^{-1} steadily shifts to higher energy with increasing pressure, while the 1935-cm^{-1} mode is comparatively pressure insensitive. The 1910-cm^{-1} band, together with the shoulder at 1904 cm^{-1}, shifts toward lower energies. The shoulder gains intensity quickly and is completley resolved with increasing pressure due to the larger negative pressure dependence. According to a factor group analysis, the e ν(CO) mode of the $Re(CO)_3$ moiety under the C_{3v} local symmetry should split into four components under C_{2h} unit cell symmetry, $2a_g + 2b_g$. In the low-pressure phase, three of the expected components are observed (Figure 2 and Table I). After the phase transition, a new peak begins to appear at 1917 cm^{-1}, which gains intensity rapidly at the expense of that at 1935 cm^{-1}. We attribute this new peak to the missing fourth factor group component associated with the e ν(CO) mode. In the high-pressure phase, where the crystal is expected to be more densely packed, the intermolecular interactions that couple the vibrational motions between the molecules in the primitive cell are strongly enhanced by pressure, resulting in stronger factor group splitting. Also, in the high-pressure phase, a redistribution of the relative intensities among all e ν(CO) related vibrations is observed. Upon application of pressure, the two bands at 1901 and 1917 cm^{-1} gain intensity, while the other two at 1911 and 1936 cm^{-1} lose intensity (Figure 2). It is known that pressure can affect Raman intensities through changes in bond polarizabilities.[14] If we assume that pressure has the same effect on the intensities of vibrations which have the same symmetry, the two bands at 1901 and 1917 cm^{-1} presumably have the same symmetry (either a_g or b_g), as do the 1911 and 1936 cm^{-1} bands.

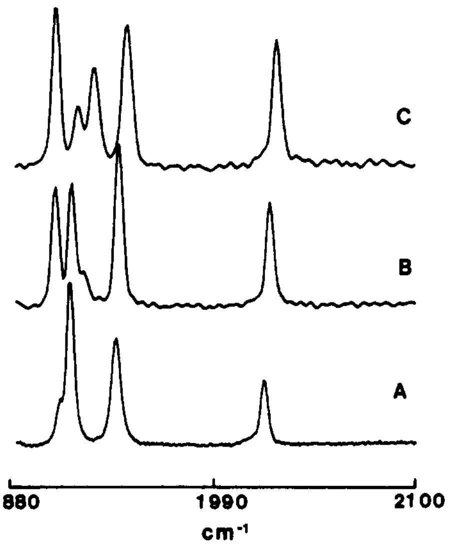

Figure 2. Micro-Raman spectra of $CpRe(CO)_3$ in the ν(CO) region at (A) 0 kbar, (B) 12.8 kbar, and (C) 23.3 kbar.

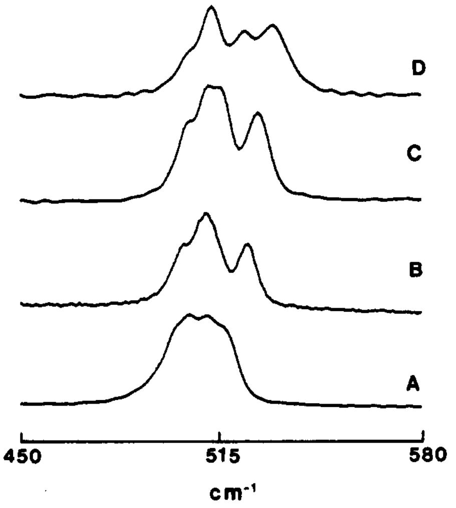

Figure 3. Micro-Raman spectra of $CpRe(CO)_3$ in the ν(ReC) region at (A) 0 kbar, (B) 6.7 kbar, (C) 12.8 kbar, and (D) 26.5 kbar.

---

[14] Sherwood, P. M. A. *Vibrational Spectroscopy of Solids*; University Press: Cambridge, U.K., 1972.

In general, most bands shift slowly with pressure toward higher wavenumbers due to the anharmonicity of the potential function. The dν/dP range for most internal stretching modes is 0.3–1.0 cm^{-1}/kbar.[15] Any abnormal behavior such as very large, small, or even a negative value for the pressure sensitivity must be discussed in terms of the particular chemical bonding involved, as well as any intra- and intermolecular interactions. In the low-pressure phase, the insensitivity or negative pressure dependences of the three e ν(CO) bands can be rationalized by using the argument put forward by Adams and his research group[1] that pressure enhances the back-bonding between the central metal and the carbonyl groups, resulting in an unchanged or decreased ν(CO) value. A comparison of the dν/dP values for the CO stretching mode with the largest negative value in several different metal carbonyl complexes leads to the following: −0.45 cm^{-1}/kbar for CpRe(CO)$_3$, which is more negative than those for CH$_3$Re(CO)$_5$ (−0.15 cm^{-1}/kbar),[5] Mn(CO)$_5$Br (−0.067 cm^{-1}/kbar),[1] or MnRe(CO)$_{10}$ (+0.16 cm^{-1}/kbar)[4] but less negative than that for CH$_3$Mn(CO)$_5$ (−0.88 cm^{-1}/kbar).[5] This relatively large negative pressure dependence is indicative of increased back-bonding. The effect of pressure on the back-bonding also depends on the nature of the other ligands bonded to the central metal. In the case of CpRe(CO)$_3$, the application of pressure apparently induces increased charge transfer from the Cp ring to the Re metal and concomitantly more extensive Re–C back-bonding. The 2016-cm^{-1} band exhibits normal pressure sensitivity, shifting steadily to higher energies, and is apparently little affected by the increased back-bonding. This observation is not too surprising, since the vibrational mode is derived from the totally symmetry a$_1$ mode of the free CpRe(CO)$_3$ molecule and this mode involves a much larger volume change than does the antisymmetric vibration. Therefore, this mode would be expected to have a large positive pressure sensitivity and this will additionally compensate for the back-bonding effect.

In the Re–C stretching region (550–400 cm^{-1}), Lokshin and co-workers reported only a broad band at 504 cm^{-1} with a shoulder at 510 cm^{-1} and assigned these peaks to the a$_1$ ν(ReC) and e ν(ReC) modes, respectively. In the present study, two broad bands are observed at 504 and 510 cm^{-1} at ambient pressure, together with a shoulder at 516 cm^{-1}. With increasing pressure, the 504 and 510 cm^{-1} bands remain stationary while the 516-cm^{-1} shoulder quickly separates from the main 510-cm^{-1} peak and is soon quite well resolved (Figure 3). This band has an unusually large positive dν/dP value (+1.22 cm^{-1}/kbar), providing further evidence that increasing pressure does lead to a strengthening in the back-bonding. This new band is attributed to the e ν(ReC) mode, contrary to the earlier assignment. The 504- and 510-cm^{-1} bands are assigned as components associated with the a$_1$ ν(ReC) mode. After the phase transition, an additional band appears at 514 cm^{-1}, presumably the result of pressure-induced factor group splitting. Because of its relatively large pressure sensitivity, this peak is most likely associated with the e ν(ReC) mode.

Drastic changes also occur in the C–H stretching region. In addition to the three previously reported bands at ambient pressure, there is a pronounced shoulder on the 3133-cm^{-1} peak. With increasing pressure, this shoulder develops into a resolved peak. After the transition, this new peak grows in intensity at the expense of the 3133-cm^{-1} peak with which it was originally associated until they finally interchange their relative intensities (Figure 4). In the high-pressure phase, the pressure dependences of both bands are nonlinear. This is typical behavior of a pressure-scanned Fermi resonance. By use of the treatment proposed by Lewis and Sherman,[16] we calculated the frequencies of two unperturbed modes which would have been seen in absence of Fermi resonance from the following equation:

$$\nu_a \text{ and } \nu_b = \tfrac{1}{2}(\nu_+ + \nu_-) + (\Delta^2 - \delta^2)^{1/2} \qquad (1)$$

where ν_+ and ν_- are the experimentally observed frequencies, $\Delta = {}^1/_2(\nu_+ - \nu_-)$, and δ = minimum value of Δ.

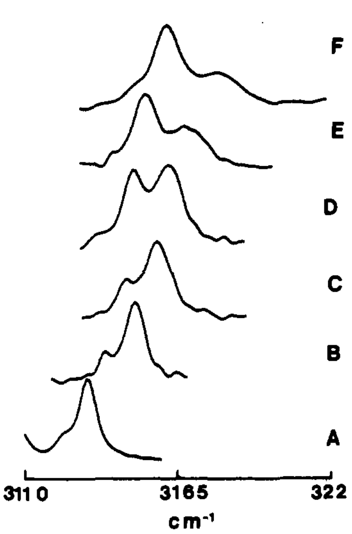

Figure 4. Micro-Raman spectra of CpRe(CO)$_3$ in the ν(CH) region at (A) 0 kbar, (B) 6.7 kbar, (C) 10 kbar, (D) 12.8 kbar, (E) 16.2 kbar, and (F) 23.3 kbar.

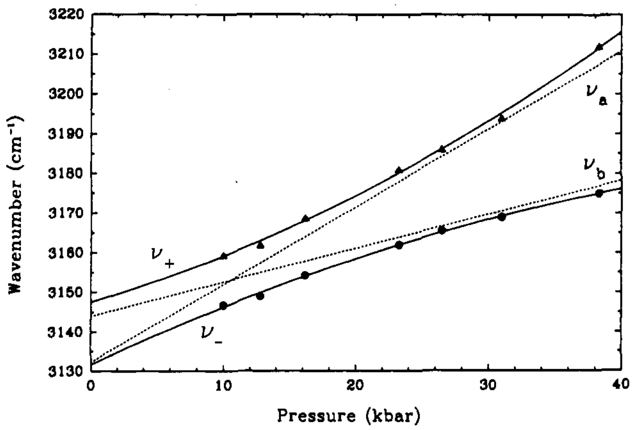

Figure 5. Pressure dependences of the Fermi resonance doublets, ν_+ and ν_-, and the calculated unmixed modes, ν_a and ν_b.

The calculated curves for ν_a and ν_b, together with the observed values for ν_+ and ν_- are shown in Figure 5. The crossover pressure at which the resonance interaction between the fundamental and combination (or overtone) reaches a maximum was calculated to be 10.9 kbar. This value is in reasonable agreement with the experimentally observed pressure of about 12.8 kbar. Since the high-frequency component of the pair (at 3133 cm^{-1}) can be identified unambiguously as an a$_1$ fundamental, the lower energy component is most probably the combination of the a$_1$ ν(CO) mode at 2016 cm^{-1} and the a$_1$ ν(CC) mode at 1107 cm^{-1}. This combination is reasonable, since interactions between the Cp ring and Re(CO)$_3$ moiety cannot be totally ignored. In the absence of Fermi resonance, the fundamental and combination would be expected, at ambient pressure, at 3144 and 3132 cm^{-1}, respectively.

The behavior of cyclopentadienyl ring vibrational modes under high pressure is similar to that for the corresponding modes of ferrocene,[17] except for the C–C stretch (e$_1$) at 1417 cm^{-1} and the C–H out-of-plane bend (a$_1$) at 825 cm^{-1}, which are totally insensitive to pressure in the low-pressure phase. The in-phase ring-breathing mode at 1107 cm^{-1} is broadened significantly with increasing pressure, as is the antisymmetric ring-breathing mode (IR-active only) in ferrocene.[18] In the latter case, it was suggested that intermolecular coupling of the vibrational motions of two molecules in the unit cell led to the corresponding Raman-active mode becoming dipole allowed. In the case of CpRe(CO)$_3$, the

---

(15) Ferraro, J. R. *Vibrational Spectroscopy at High External Pressures: The Diamond Anvil Cell*; Academic Press: Orlando, FL, 1984.

(16) Lewis, S.; Sherman, W. F. *Spectrochim. Acta* **1979**, *35A*, 613.

(17) Adams, D. M.; Williams, A. D. *J. Phys. Chem. Solids* **1980**, *41*, 1073.

(18) Roginski, R. T.; Shapley, J. R.; Drickamer, H. G. *J. Phys. Chem.* **1988**, *92*, 4316.

symmetric ring-breathing mode should split into four components ($a_g + b_g + a_u + b_u$) under C_{2h} unit cell symmetry, the g and u modes being Raman and IR active, respectively. This splitting was not observed at ambient pressure, however, indicating that the intermolecular coupling between the molecules in the unit cell is weak but may be increased by applying pressure, eventually resulting in the observed peak broadening. The origin of the coupling may arise from the ring-ring interaction, which has been calculated to be the largest contributor to the intermolecular interaction at ambient pressure.[6] Very recently, Coffer and coworkers[19] have examined the high-pressure IR spectra of a series of C_2 hydrocarbon ligands coordinated to a triosmium framework and found that the values of $d\nu/dP$ follow the order: C–H stretching > C–C stretching > C–H bending. In our study of $CpRe(CO)_3$, no such conclusion could be drawn owing to the complex spectrum of the Cp ligand.

The pressure dependence of the ring tilt at 349 cm^{-1} is twice that of the antisymmetric ring tilt in ferrocene.[17] High-pressure IR studies of some metal-sandwich compounds by Nakamoto and co-workers[20] have indicated that the metal-ring stretching vibration is more pressure sensitive than is the ring tilt vibration. However, these two vibrations have almost same $d\nu/dP$ value in $CpRe(CO)_3$.

All values of the relative pressure sensitivity, $d \ln \nu/dP$, are typical of those found for internal vibrational modes except for three bands initially at 129 cm^{-1} (Cp–Re–$(CO)_3$ bending (e)), 114 cm^{-1} (C–Re–C bending (e)), and 100 cm^{-1} (C–Re–C bending (a_1)). These three internal modes shift with increasing pressure at rates much faster than normal. The large $d \ln \nu/dP$ value of some low-frequency internal modes may result from the coupling with external modes. However, according to Chhor and Lucazeau,[10] this does not occur for $CpRe(CO)_3$. The C–Re–C bending vibrations are expected to be less sensitive than the corresponding stretching vibrations because they are less affected by the volume change of crystal. But the reverse is observed in our work. It is possible that the larger $d \ln \nu/dP$ values for the C–Re–C bending modes may result from slight changes in the C–Re–C angles upon application of pressure from its average value of 90°,[8] because a pressure-induced angle change will certainly increase the restoring potential and at the same time the energy of the bending mode. As pointed out by Elian and co-workers,[21] the (O)C–M–C(O) angle in such a system is extremely sensitive to the extent of mixing between the carbonyl molecular orbitals and to the nature of the other ligands present. If it is again considered that pressure facilitates electron density transfer from the Cp ring to the Re metal, then the C–Re–C angle should become larger with increasing pressure.

Acknowledgment. This research work was generously supported by grants from the NSERC and CANMET (Canada) and the FCAR (Quebec). Y.H. acknowledges the award of a graduate fellowship from McGill University.

---

[19] Coffer, J. L.; Drickamer, H. G.; Park, J. T.; Roginski, R. T.; Shapley, J. R. *J. Phys. Chem.* **1990**, *94*, 1981.

[20] Nakamoto, K.; Udovich, C.; Ferraro, J. R.; Quattrochi, A. *Appl. Spectrosc.* **1970**, *24*, 606.

[21] Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.

Contribution from the Institut für Anorganische Chemie der Universität,
Auf der Morgenstelle 18, D-7400 Tübingen 1, West Germany

Phosphorus-31 Solid-State NMR Studies of Cyclic and Acyclic Phosphine–Metal Complexes. Determination of Chemical Shift Anisotropy, Scalar Coupling $^1J_{M-P}$ (M = ^{55}Mn, $^{95/97}$Mo, ^{183}W), and ^{55}Mn Quadrupolar Coupling Constants

Ekkehard Lindner,* Riad Fawzi, Hermann August Mayer, Klaus Eichele, and Klaus Pohmer

Received June 28, 1990

The ^{31}P chemical shift tensors of cyclic and acyclic metal phosphine complexes of the type $[M]PPh_2R$ ($[M] = (OC)_4BrMn$ (**1**), $Cp(OC)_2ClW$ (**2**), $Cp(OC)_2MeW$ (**3**); R = Et (**a**), Pr (**b**), Bu (**c**), Pe = Pentyl (**d**)) and $\overline{[M]PPh_2(C}H_2)_n$ ($[M] = (OC)_4Mn$ (**4**), $Cp(OC)_2W$ (**5**), $Cp(OC)_2Mo$ (**6**); n = 3 (**b**), 4 (**c**); $[M] = (OC)_4MnSO_2$ (**7**); n = 2 (**b**), 3 (**c**), 4 (**d**)) are determined by solid-state NMR techniques and correlated to structural features of the compounds. In general the isotropic chemical shift in the solid-state was found to be of the same order as the chemical shift in solution. There are differences in the tensor components due to structural changes for the manganese complexes **1**. Different bond weakening abilities of a ligand (trans influence) in complexes **2** and **3** cause a large change of only one tensor component, while the other components remain constant. A "crossover" of the center shielding tensor component and the low-field component is observed for the five- and six-membered rings **4b**–**7b** and **4c**–**7c**, respectively. ^{55}Mn- and $^{95/97}$Mo–^{31}P coupling constants have been observed that are not obtainable in solution. The different spacings within the multiplets of the ^{31}P CP/MAS spectrum of the manganese complex **1d** allows us to estimate the quadrupolar coupling constant χ and the asymmetry parameter η of the electric field gradient at manganese.

Introduction

Today high-resolution ^{31}P NMR spectroscopy in solution is a widely used method with manifold applications in the observation of changes in bonding and stereochemistry of phosphorus compounds.[1] In these studies the diagnostic manner in which the spectra reflect the local environments of the nuclei is a key feature. Generally, a correlation of spectral information to structural details is difficult. Within a series of mutually related compounds, the problems are reduced in a first approximation to one structural parameter as the major contributor that determines the spectrum. In this way it is possible to correlate $\delta(^{31}P)$ empirically with various parameters. Examples are the definition of group contributions to the chemical shift of phosphines,[2] the coordination shift $\Delta\delta$ on complexation of phosphines to metal fragments,[3] the dependence of $\delta(^{31}P)$ in complexes on the cone angle of the ligand,[4] and the ring contribution Δ_R for phosphorus atoms involved in chelate rings.[5]

The last effect, in particular, has been well-known since one of the first publications about ^{31}P NMR studies on organometallic compounds.[6] Later investigations showed a clear dependence of

---

[1] *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, FL, 1987.

[2] Grim, S. O.; McFarlane, W.; Davidoff, E. F. *J. Org. Chem.* **1967**, *32*, 781.

[3] Mann, B. E.; Masters, C.; Shaw, B. L.; Slade, R. M.; Stainbank, R. E. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 881.

[4] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[5] Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

0020-1669/91/1330-1102$02.50/0