Effect of High External Pressures on the Infrared and Micro-Raman Spectra of Crystalline, Octahedral Mixed Carbonyl−*tert*-Butyl Isocyanide Complexes of Chromium(0)

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Infrared and micro-Raman spectra of crystalline $Cr(CO)_5(CNBu-t)$ and *cis*-$Cr(CO)_4(CNBu-t)_2$ have been recorded in the 3000−390 cm^{-1} region at ambient temperature and selected pressures up to 45 kbar with the aid of diamond-anvil cells. The vibrational data indicate that both the mono- and the disubstituted complex undergo a phase transition (possibly second order) at ∼11 and ∼6 kbar, respectively. The ν(CN) modes are significantly more pressure sensitive in the low-pressure phases than are the ν(CO) modes. The pressure dependences ($d\nu/dP$) in the high-pressure phases are similar. The Cr−CO and Cr−CNBu-*t* π-back-bonding interactions are apparently increased in the low-pressure phases by the application of pressure. This effect is greatest for the CO ligands, affording additional evidence for the weaker π-acceptor capacity of the CNBu-*t* ligand. This interpretation is supported by the fact that the ν(CO) modes involving vibrations of CO groups *trans* to CNBu-*t* have significantly higher pressure dependences than do the other ν(CO) vibrations. High-pressure vibrational spectroscopy is another useful way of probing the relative π-back-bonding capabilities of different π-acid ligands in organometallic complexes.

Introduction

Vibrational spectroscopy has played a pivotal role in the structural identification of organometallic compounds over the past 50 years. The spectral data have provided important information about the molecular and crystal structures of the complexes as well as about the nature of the chemical bonding involved.[1−3] The earlier work was often concerned with structural changes which could be detected spectroscopically upon going from solution to the solid state and the effect of temperature on these changes. Solid materials also often undergo dramatic structural changes when subjected to high external pressures. These changes encompass pressure-induced phase transitions and/or geometrical, conformational, and spin-state transformations, etc.[4−6] The application of pressure is an important way of changing interatomic and intermolecular distances in solids without significantly perturbing any other parameters. Much of our recent research has been directed at investigating the effects of high external pressures on the vibrational spectra of organic and organometallic molecular crystals. These measurements are performed with the aid of commercial variable-pressure diamond-anvil cells (dacs).

Previous studies of the vibrational spectra of organometallic complexes at high pressures in dacs have demonstrated the existence of first- and second-order pressure-induced phase transitions in some of these materials.[6,7] For example, there is a first-order transition in $Re_2(CO)_{10}$ at ∼8 kbar,[8] while $W(CO)_6$

and $Mn(CO)_5Br$ exhibit second-order transitions at 16 and ∼24 kbar, respectively.[9,10] These pressure-tuning experiments have also provided some information on the π-back-bonding in organometallic complexes containing π-acid ligands such as CO,[9] CS,[11] and C_2H_4.[12] In this paper, we report the results of the first high-pressure IR and micro-Raman spectroscopic study of organometallic complexes containing another type of π-acid ligand, *viz.*, *tert*-butyl isocyanide in $Cr(CO)_5(CNBu-t)$ and *cis*-$Cr(CO)_4(CNBu-t)_2$. These high-pressure vibrational measurements can provide additional insight into the relative π-back-bonding capabilities of different π-acid ligands.

Experimental Section

Materials. The chromium(0) complexes, $Cr(CO)_5(CNBu-t)$ and *cis*-$Cr(CO)_4(CNBu-t)_2$, were prepared and purified by the literature methods.[13]

Vibrational Spectra. The IR spectra (2 cm^{-1} resolution) were acquired on a Bruker IFS-48 FT spectrometer equipped with a liquid N_2-cooled MCT-D326 detector. The dac for the IR studies was purchased from High Pressure Diamond Optics (Tucson, AZ) and was fitted with type IIA diamonds. The antisymmetric NO stretching mode of $NaNO_3$ in a dilute NaBr matrix (∼5%) was used as the pressure calibration peak.[14] A circular gasket was placed between the faces of the two diamonds in the dac in order to ensure there was as uniform a pressure gradient as possible across the faces.[4] The gasket was cut from a 200 μm thick stainless-steel plate and had a 400 μm diameter

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(1) Adams, D. M. *Metal-Ligand and Related Vibrations*; Edward Arnold Ltd.: London, 1967.
(2) Nakamoto, K. *Infrared and Raman Spectra of Inorganci and Coordination Compounds*, 4th ed.; John Wiley & Son: New York, 1986.
(3) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.
(4) Sherman, W. F.; Wilkinson, G. R. In *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Heyden and Son: London, 1980; Vol. 6.
(5) Wong, P. T. T. In *Vibrational Spectroscopy and Structure: A Series of Advances*; Durig, J. R., Ed.; Elsveier: Amsterdam, 1987; Vol. 16.
(6) Ferraro, J. R. *Vibrational Spectroscopy at High External Pressures: The Diamond Anvil Cell*; Academic Press: Orlando, FL, 1984.

(7) Adams, D. M.; Davey, L. M.; Hatton, P. D.; Shaw, A. C. *J. Mol. Struct.* **1982**, *79*, 415.
(8) Adams, D. M.; Ekejiuba, I. O. C. *J. Chem. Phys.* **1983**, *78*, 5408.
(9) Adams, D. M.; Ekejiuba, I. O. C. *J. Chem. Phys.* **1982**, *77*, 4793.
(10) Huang, Y.; Butler, I. S.; Gilson, D. F. R.; Lafleur, D. *Inorg. Chem.* **1991**, *30*, 117.
(11) Huang, Y. Butler, I. S.; Gilson, D. F. R. *Spectrochim. Acta* **1991**, *47A*, 909.
(12) Baldwin, J.; Butler, I. S.; Gilson, D. F. R. In *Proceedings of 27th Annual Meeting of Microbeam Analysis Society*; Bailey, G. W., Bentley, J., Small, J. A., Eds.; San Francisco Press Inc.: San Francisco, CA, 1992; p 1536. See also: Baldwin, J. M.Sc. Thesis, McGill University, Montreal, Quebec, Canada, 1992.
(13) Albers, M. O.; Coville, N. J. *Inorg. Synth.* **1990**, *28*, 140.
(14) Klug, D. D.; Whalley, E. *Rev. Sci. Instrum.* **1983**, *54*, 1205.

hole drilled in the center to hold the sample and the pressure calibrant. No pressure-transmitting fluid was used because both complexes were soluble in those most commonly employed. The gasket was loaded with the aid of a conventional optical microscope. The dac was placed directly under the 15× objective of a Bruker IR microscope interfaced to the spectrometer, and spectral alignment was achieved by means of a Sony color video camera (Model DXC-107) mounted on the IR microscope coupled to a Sony color video monitor (Model PVM-1340).

The micro-Raman spectra (2 cm^{-1} resolution) were recorded 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 argon ion (5 W) laser was used to excite the spectra; the laser power employed at the samples was typically ~30 mW. A 400 μm thick stainless-steel circular gasket was placed between the faces of the opposing diamonds in the dac (Diacell Products, Leicester, U.K.). The pressure was determined by monitoring the pressure dependence of the R$_1$ fluorescence line of ruby.[15] The sample and a tiny ruby chip were carefully loaded into the 300 μm hole at the center 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 the a 4× microscope objective. The backscattered radiation was also collected through the same objective. No high-pressure Raman data could be obtained for the lattice region (<200 cm^{-1}) because of interference from the strong laser-induced fluorescence background of the diamonds in the dac.

Results and Discussion

Detailed vibrational assignments have been already proposed for the ambient-temperature and -pressure IR and Raman spectra of the group 6B metal complexes M(CO)$_{6-n}$(CNBu-t)$_n$ (M = Cr, Mo, W; n = 1−3).[16] From these results, together with those from related NMR spectroscopic studies,[17] CNBu-t is considered to be a better σ-donor but poorer π-acceptor ligand than CO. The extent of π-back-bonding between a transition metal and a π-acid ligand can be altered appreciably by the application of pressure. Therefore, the pressure dependences (dν/dP) for the ν(CN), ν(CO), ν(Cr−CO) and ν(Cr−CN) modes in Cr(CO)$_5$-(CNBu-t) and cis-Cr(CO)$_4$(CNBu-t)$_2$ should reflect principally the differences in the π-back-bonding capabilities of the CNBu-t and CO ligands, bearing in mind that differences in the Cr−CN and Cr−CO σ-bonding capabilities may also have some slight effect. Moreover, since there are band overlaps and vibrational coupling in the low-energy region between the metal-carbon stretching [ν(Cr−CO) and ν(Cr−CN)] and linear bending modes [δ(CrCO) and δ(CrCN)] at ambient pressure, the pressure behavior of these various modes may aid in their assignment.[10,18]

Phase Transitions. At ambient temperature and pressure, several of the IR- and Raman-active fundamentals of solid Cr-(CO)$_5$(CNBu-t) and cis-Cr(CO)$_4$(CNBu-t)$_2$ are split,[16] but these splittings do not seriously affect the proposed assignments. The strongest IR and Raman bands of the two complexes were examined at various pressures approaching 40 kbar. Examples of the band shifts observed with increasing pressure for several of the vibrational modes are illustrated in Figures 1−4.

Any solid material will eventually undergo structural changes, provided that high enough pressures are applied. Moreover, since pressure-induced phase transitions normally proceed in the direction of greater packing efficiency, less efficiently packed structures are more likely to undergo pressure-induced structural changes. In the case of Cr(CO)$_5$(CNBu-t) and cis-Cr(CO)$_4$-(CNBu-t)$_2$, the CNBu-t ligand is appreciably bulkier than is CO and room-temperature X-ray diffraction studies have shown that both complexes are disordered in the solid state.[19,20] There are
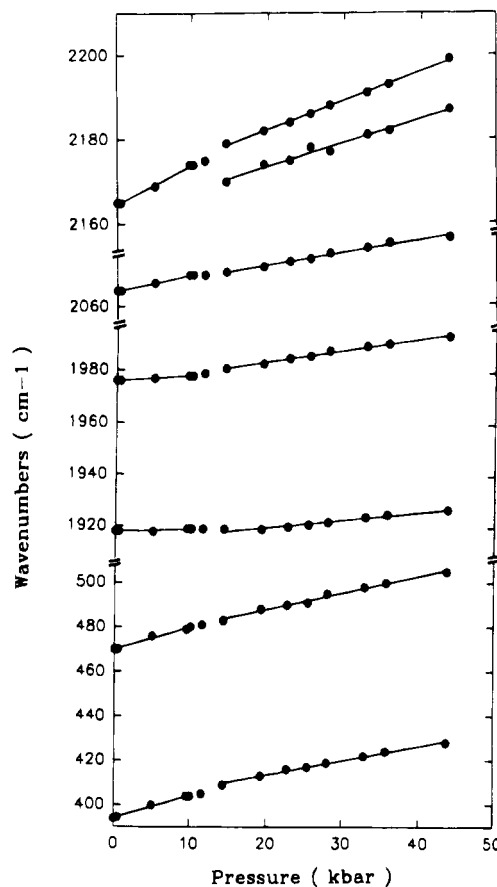

Figure 1. Pressure dependences of selected Raman bands of Cr(CO)$_5$-(CNBu-t).
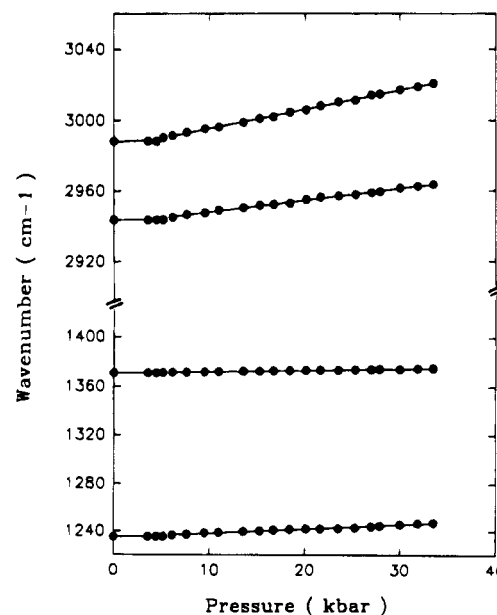

Figure 2. Pressure dependences of selected IR bands of Cr(CO)$_5$-(CNBu-t).

large "liquid-like" motions associated primarily with the CNBu-t ligands, presumably because of their larger volume. The mixed-ligand chromium(0) derivatives would therefore be much more likely to undergo pressure-induced structural changes than would the parent Cr(CO)$_6$ molecule.[21]

(15) Barnett, J. D.; Block, S.; Piermarini, G. J. *Rev. Sci. Instrum.* **1973**, *44*, 1.
(16) Li, H.; Butler, I. S.; Uhm, H. L. *J. Raman Spectrosc.* **1992**, *23*, 457.
(17) Minelli, M.; Maley, W. J. *Inorg. Chem.* **1989**, *28*, 2954.
(18) Lewis, S.; Sherman, W. F. *Spectrochim. Acta* **1979**, *35A*, 613.
(19) Li, H.; Butler, I. S. *Inorg. Chim. Acta*, submitted for publication.
(20) Clegg, W.; Klingebiel, U.; Sheldrick, G. M. *Z. Naturforsch.* **1983**, *38B*, 260.
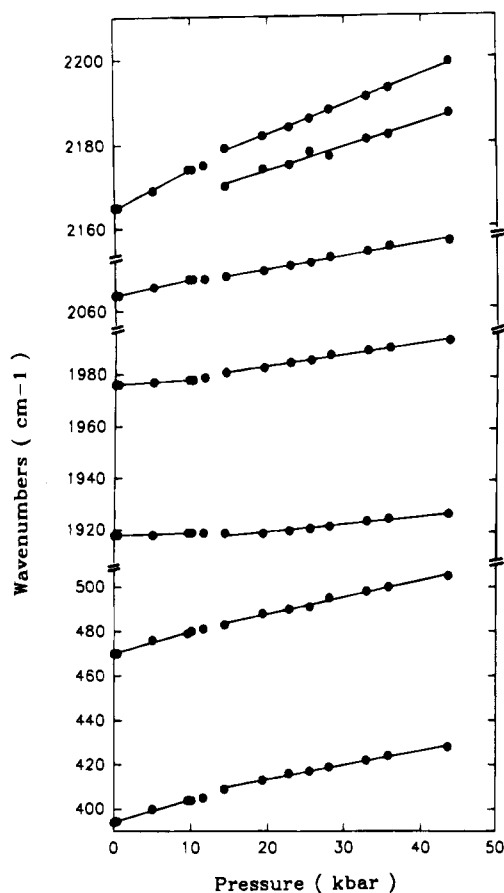
Figure 3. Pressure dependences of selected Raman bands of Cr(CO)₄-(CNBu-*t*)₂.

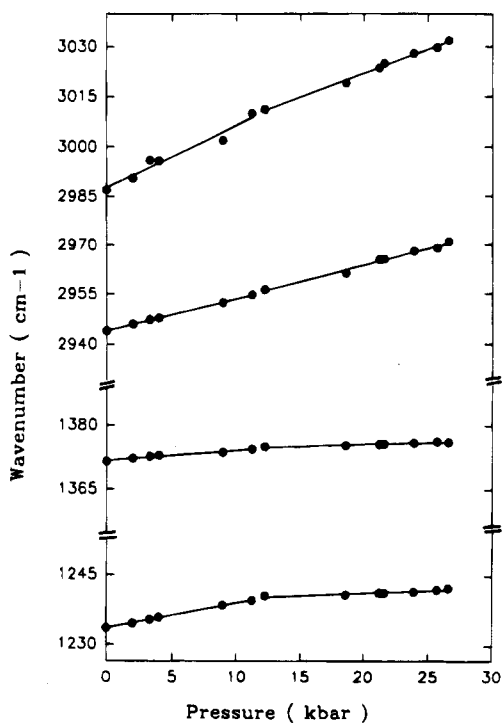**Figure 4.** Pressure dependences of selected IR bands of Cr(CO)₄-(CNBu-*t*)₂.

Many of the observed IR and Raman bands exhibit discontinuities in the ν vs P plots at ~11 kbar for Cr(CO)₅(CNBu-*t*)

(21) Rao, C. N. R.; Gopalakrishnan, J. *New Directions in Solid State Chemistry*; Cambridge University Press: London, 1986.

**Table 1.** Pressure Dependences of the Principal IR and Raman Bands of Cr(CO)₅(CNBu-*t*)

low-pressure phase			high-pressure phase			
ν, cm⁻¹	dν/dP, cm⁻¹/ kbar	d ln ν/dP, kbar⁻¹ × 10⁻³	ν, cm⁻¹	dν/dP, cm⁻¹/ kbar	d ln ν/dP, kbar⁻¹ × 10⁻³	assign
2987.8	1.9	0.60	2993.3	1.4	0.50	ν(CH)asym
2944.5	0.90	0.30	2945.4	1.0	0.30	ν(CH)sym
2164.0	0.90	0.40	2169.0	0.70	0.30	a₁ ν(CN)
			2163.0	0.60	0.30	
2066.0	0.60	0.30	2072.0	0.50	0.24	a₁^{eq} ν(CO)
1976.0	0.10	0.05	1978.0	0.50	0.25	b₁ ν(CO)
1918.0	0.10	0.05	1919.0	0.30	0.15	a₁^{ax} ν(CO)
1372.2	0.20	0.10	1374.7	0.10	0.07	δ(CH₃)
1234.5	0.50	0.40	1239.8	0.10	0.08	δ(CH₃)
470.0	1.0	2.1	474.0	0.80	1.7	ν(Cr–CO)
394.0	1.0	2.5	401.0	0.60	1.5	ν(Cr–CO)

Table 2. Pressure Dependences of the Principal IR and Raman Bands of *cis*-Cr(CO)₄(CNBu-*t*)₂

low-pressure phase			high-pressure phase			
ν, cm⁻¹	dν/dP, cm⁻¹/ kbar	d ln ν/dP, kbar⁻¹ × 10⁻³	ν, cm⁻¹	dν/dP, cm⁻¹/ kbar	d ln ν/dP, kbar⁻¹ × 10⁻³	assign
2989.2	0.26	0.09	2992.5	1.1	0.36	ν(CH)$_{asym}$
2943.5	0.01	0.003	2945.5	0.67	0.23	ν(CH)$_{sym}$
2160.0	2.1	0.97	2172.0	0.92	0.42	a₁ ν(CN)
			2167.0	0.81	0.37	
2134.0	2.0	0.91	2148.0	1.1	0.49	b₁ ν(CN)
			2141.0	0.68	0.32	
2007.0	0.90	0.45	2012.0	0.56	0.28	a₁ ν(CO)
1935.0	0.20	0.10	1937.0	0.50	0.26	
1922.0	0.99	0.50	1927.0	0.63	0.33	b₁ ν(CO)
1920.0	0.00		1920.0	0.35	0.18	
1909.0	0.21	0.11	1910.0	0.52	0.27	a₁ ν(CO)
1901.0	0.00		1901.0	0.41	0.22	
1881.0	0.00		1880.0	0.22	0.12	
1874.0	0.00		1875.0	0.29	0.15	b₂ ν(CO)
1870.0	0.00		1871.0	0.38	0.20	
1371.2	0.03	0.02	1372.5	0.14	0.10	
1235.4	0.03	0.02	1237.8	0.36	0.29	δ(CH₃)
730.0	0.18	0.25	734.0	0.78	1.1	
673.0	0.40	0.59	676.0	0.20	0.30	δ(Cr–CO)
659.2	0.59	0.89	662.0	0.39	0.59	
476.0	0.76	1.6	490.0	0.68	1.4	ν(Cr–CO)
			479.0	0.23	0.48	
429.0	0.20	0.47	430.0	0.44	1.0	δ(CrCN)
398.0	1.3	3.3	409.0	0.77	1.9	ν(Cr–CO)
			403.0	0.75	1.9	

(Figures 1 and 2) and at ~6 kbar for *cis*-Cr(CO)₄(CNBu-*t*)₂ (Figures 3 and 4). Such discontinuities are good indicators of pressure-induced phase transitions.[7–9] While the numbers of bands observed before and after the onset of the discontinuities remain the same for both the mono- and disubstituted complexes, there are a few splittings detected as the pressure is increased. These splittings appear gradually over a range of pressures and are not associated with any abrupt phase transition. There are also some slight changes in slope detected in the ν vs P plots before and after the onset of the discontinuities. These results could be explained by the occurrence of a second-order pressure-induced phase transition in each compound. Alternatively, since there are pressure and shear gradients across the gasket hole and within individual crystallites in a nonhydrostatic medium, a first-order phase transition may be taking place which is smeared out over a range of average pressures. The measured pressure dependences (dν/dP) and relative pressure dependences (d ln ν/dP) for the two phases of Cr(CO)₅(CNBu-*t*) and *cis*-Cr(CO)₄(CNBu-*t*)₂ are given in Tables 1 and 2, respectively.

Micro-Raman Spectra. (a) ν(CO) and ν(CN) Modes (2200–1800 cm⁻¹ Region). On the basis of C_{4v} point group
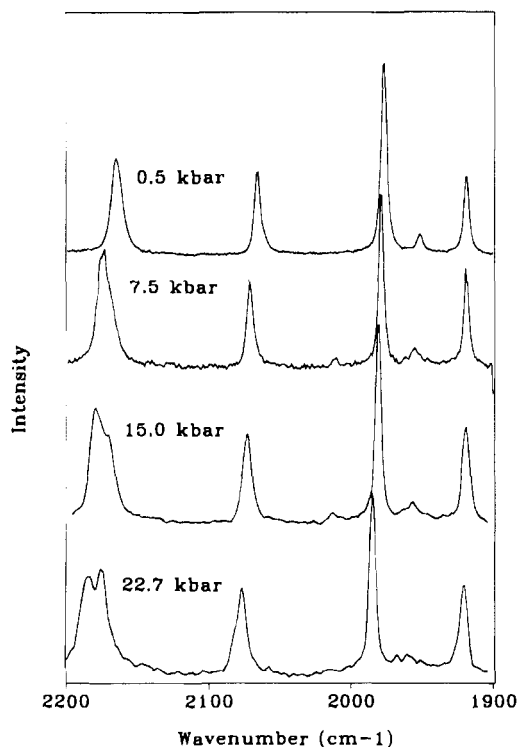
Figure 5. Raman spectra of Cr(CO)₅(CNBu-*t*) in 2200–1900 cm⁻¹ region.

symmetry for the Cr(CO)₅(CNBu-*t*) complex, the group theoretical predictions for the ν(CO) modes are 2a₁(IR/Raman) + b₁ + e(IR/Raman). No marked solid-state splitting of any these modes is observed in the Raman spectrum at ambient pressure. At room-temperature, Cr(CO)₅(CNBu-*t*) crystallizes in the monoclinic space group *P*2₁/*a* (isomorphous with *P*2₁/*b* or *P*2₁/*c*, *C*₂ₕ⁵) with four molecules per unit cell located at *C*₁ sites.[19] From correlation between the *C*₄ᵥ molecular the *C*₁ site and the *C*₂ₕ factor group symmetries, the a₁ and b₁ modes should split into doublets in both the Raman and the IR, while the doubly-degenerate e mode should give rise to quartets in both types of spectra. At ambient pressure, however, none of these predicted splittings is detected. For many molecular crystals, such factor group splittings only really emerge at higher pressures.[22] In the case of Cr(CO)₅(CNBu-*t*), a distinct shoulder appears on the lower energy side of the Raman-active a₁ ν(CN) mode (2164.0 cm⁻¹) at ~9 kbar. This splitting continues until both components are fully resolved at ~21 kbar (Figure 5). At even higher pressures, the intensities of the two components are interchanged. In addition, the a₁ᵉ𝑞 ν(CO) mode exhibits a discernible shoulder in the Raman spectrum of the high-pressure phase. The e ν(CO) mode is quite weak in the Raman, but there is some evidence for splitting into two components at ~10 kbar.

In the low-pressure phase of Cr(CO)₅(CNBu-*t*), the a₁ᵉ𝑞 ν-(CO) mode is appreciably more pressure sensitive than are the a₁ᵃˣ and b₁ ν(CO) modes, which are essentially independent of pressure. Immediately following the second-order phase transition, all three ν(CO) modes begin to shift to higher energies with about the same pressure sensitivity (Table 1). The CN bond is apparently much more compressible in both the low- and high-pressure phases than are the CO bonds, possibly because of the greater anharmonicity⁶ of the ν(CN) vibration and larger bulk of the CNBu-*t* ligand. The pressure dependences of vibrational modes depend chiefly on the nature of the

(22) Haines, J.; Gilson, D. F. R. *J. Phys. Chem.* **1989**, *93*, 7920.

chemical bonding and the anharmonicities involved in the modes, as well as the relative orientations of the molecules in the unit cell of the crystal.⁴ The application of external pressure to a crystal lattice leads to compression of the unit cells, ultimately resulting in increases in the energies of all the vibrational modes. Most vibrational modes therefore shift to higher wavenumbers with increasing pressure because of the increased interatomic and intermolecular interactions occurring since the separations are becoming smaller and consequently the force constants are being increased. The Cr–C(O) [and Cr–C(N)] force constants would therefore be expected to increase with increasing pressure. However, as pointed out originally by Adams and Ekejiuba,⁸,⁹ the strengthening of the M–CO bonds in metal carbonyls also results from the increased π-back-bonding between the metal M and the π*-orbitals of the CO ligands. Any increase in the extent of π-back-bonding will lead to a reduction in the force constants of the CO bonds. The observed pressure dependences of the ν(CO) modes could thus be the net result of primarily these two opposing effects, remembering, of course, that the M–CN and M–CO σ-bonding may play a slight role as well.²³ The fact that the a₁ᵃˣ and b₁ ν(CO) modes in Cr(CO)₅(CNBu-*t*) have very low pressure dependences is in agreement with this explanation. The ν(CN) mode has a much greater pressure dependence in the low pressure-phase than do the ν(CO) modes, providing further evidence for the poorer π-acceptor capacity of the CNBu-*t* ligand. Since there is less π-back-bonding, most of the pressure effect is associated with the Cr–CO bonds rather than the Cr–CN bond. Furthermore, the pressure dependence of the a₁ᵉ𝑞 ν(CO) mode in the low-pressure phase is greater than that for the a₁ᵃˣ ν(CO) mode, suggesting that the geometrical position of the CNBu-*t* ligand may also play a role in the pressure behavior of the different vibrational modes. The a₁ᵃˣ ν(CO) mode in Cr(CO)₅(CNBu-*t*) is due primarily to vibration of the CO group *trans* to the CNBu-*t* ligand, and this vibration is much more likely to be affected by the presence of the bulky isocyanide ligand than are the four equatorial CO groups. It is certainly already well-known that the steric bulk of the CNBu-*t* ligands is important in synthetic chemistry since only *cis*- and *fac*-isomers have thus been isolated from the CO substitution reactions of M(CO)₆ with CNBu-*t*.¹⁷

A room-temperature X-ray diffraction study has shown that *cis*-Cr(CO)₄(CNBu-*t*)₂ crystallizes in the orthorhombic space group *Pccn* (*D*₂ₕ¹⁰) with four molecules per unit cell.²⁰ Since the molecular symmetry of the molecule is *C*₂ᵥ, the site symmetry must be either *C*₂ or *C*ᵢ. However, the coincidence of many of the IR and micro-Raman bands does not support the presence of a center of symmetry and so the *C*₂ site group is more likely. From a factor group analysis, each of the four IR-/Raman-active ν(CO) modes (2a₁ + b₁ + b₂) should be split into two components in the Raman spectrum of the crystal. The b₁ and b₂ ν(CO) bands do display slight shoulders at ambient pressure, while at higher pressures, these bands are definitely resolved into two distinct components (Figure 6). Neither of the predicted ν(CN) modes (a₁ + b₁) exhibits any splitting at ambient pressure, but the two modes have quite large pressure dependences in both pressure phases similar to that for the ν-(CN) mode in the monosubstituted complex. Both modes show factor group splitting at ~4 kbar. Why the ν(CN) modes in the mono- and disubstituted complexes do not exhibit any significant factor group splitting at ambient pressure is most

(23) Complete normal-coordinate calculations on the effects of high pressures on the force constants in selected metal carbonyl complexes are currently underway (Mink, J.; Butler, I. S. Unpublished results). The results of these calculations should lead to a better understanding of the bonding properties affected.
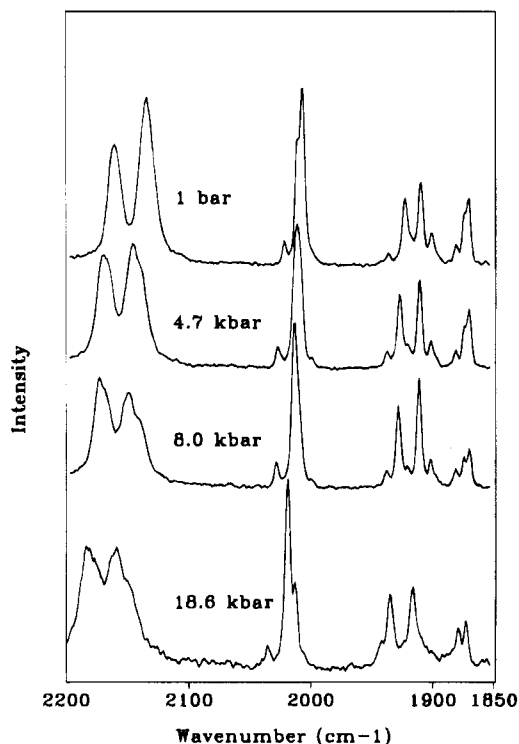
Figure 6. Raman spectra of Cr(CO)₂(CNBu-*t*)₂ in 2200—1850 cm⁻¹ region.

probably related to the large thermal motions of the bulky *tert*-butyl groups in the crystals. The methyl groups in some typical molecular crystals[24] have large thermal rotational motions, even at ~100 K, at which temperatures the crystals are highly contracted. A similar kind of thermal motion might blur the factor group splitting components of the associated ν(CN) modes at ambient pressure. When the applied pressure is increased, however, these thermal motions become more restricted and the factor group splittings can be discerned. Finally, the CO stretching modes of *cis*-Cr(CO)₄(CNBu-*t*)₂ can be divided into vibrations involving CO groups either *cis* or *trans* to the CNBu-*t* ligands. In the low-pressure phase, the ν(CO) modes for the CO groups *trans* to the CNBu-*t* ligands, i.e., the a₁⁽²⁾ and b₂ modes, would be expected to exhibit greater π-back-bonding effects. This means that these modes should have smaller pressure dependences than do those of the a₁⁽¹⁾ and b₁ ν(CO) modes, which are due to vibrations of the CO groups that are *cis* to the CNBu-*t* ligands. These predictions are confirmed by the pressure dependence data given in Table 2 and Figure 2.

(b) Low-Energy Vibrations. On the basis of complete normal-coordinate calculations for M(CO)₆ and [M(CN)₆]³⁻ (M = Cr, Mo, W),[25-27] the δ(CrCO), δ(CrCN), ν(Cr—CO), and ν(Cr—CN) modes of the mixed carbonyl—*tert*-butyl isocyanide complexes should appear in the 700—300 cm⁻¹ region. Since the energy differences between these four kinds of vibrations are quite small, there is a strong tendency for band overlapping and vibrational coupling in this region.[28,29] The vibrational

(24) Larsen, D. W.; Soltz, B. A.; Stary, F. E.; West, R. *J. Phys. Chem.* **1980**, *84*, 1340.

(25) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349.

(26) Caglioti, V.; Sartori, G.; Scrocco, M. *J. Inorg. Nucl. Chem.* **1958**, *8*, 87.

(27) Bigorgne, M. *J. Organomet. Chem.* **1963**, *1*, 101.

(28) Adams, D. M. *J. Chem. Soc.* **1964**, 1771.

(29) Chalmers, A. A.; Lewis, J.; Whyman, R. *J. Chem. Soc.* **1967**, 1871.

spectra of the mixed-ligand complexes are more complicated than are those of M(CO)₆ and [M(CN)₆]³⁻. Only two relatively strong ν(Cr—CO) Raman bands at 470 and 394 cm⁻¹ could be easily monitored for Cr(CO)₅(CNBu-*t*) under high pressure. Both bands shift toward higher energies much faster in the low-pressure phase with increasing pressure than do the ν(CO) modes. In the high-pressure phase, these bands are only slightly pressure sensitive. These experimental observations are consistent with the anticipated increased π-back-bonding interactions between Cr and the CO ligands with increasing pressure.

In the case of *cis*-Cr(CO)₄(CNBu-*t*)₂, the two medium-intense bands at 673.0 and 657.0 cm⁻¹ and the two strong bands at 476.0 and 398.0 cm⁻¹ have been attributed to a δ(CrCO) and a ν(Cr—CO) mode, respectively. It is difficult to decide *a priori* if the 428 cm⁻¹ band should be assigned to a ν(Cr—CN) or a δ(CrCN) mode. Generally speaking, bending vibrations are less affected by pressure than are stretching vibrations. A typical value for internal bond stretching is 0.3—1.0 cm⁻¹/kbar, while that for a bending mode is 0.1—0.3 cm⁻¹/kbar.[6] The 428.0 cm⁻¹ band has pressure dependences in both phases (Table 2) which correspond more to a bending than a stretching vibration and so we have assigned this band to δ(CrCN). The relative intensities of the ν(Cr—CO) mode at 398.0 cm⁻¹ and the δ-(CrCN) mode at 428.0 cm⁻¹ are reversed in the high-pressure phase. This intensity reversal is possibly the result of vibrational coupling in which the ν(Cr—CO) mode borrows intensity from the δ(CrCN) mode at ambient pressure, but when the pressure becomes high enough to break the vibrational coupling, the intensity reverts back to the δ(CrCN) mode. Finally, the two strong ν(Cr—CO) bands also show factor group splitting at ~4 kbar.

High-Pressure Infrared Spectra. Despite the fact that the ν(CO) and ν(CN) modes are buried beneath the intense IR absorption near 2000 cm⁻¹ due to the diamonds in the dac, it is still possible to extract some useful information from pressure-tuning IR measurements. In particular, the pressure behavior of the ν(CH) stretching and the δ(CH₂) and δ(CH₃) deformation modes in the CNBu-*t* ligands can be examined quite easily. The ν(CH) region is especially important because no data can be obtained for this region from the complementary Raman measurements because of the strong diamond fluorescence near 3000 cm⁻¹.

The effect of pressure could only be examined for the strong IR-active symmetric and antisymmetric ν(CH) modes of the CH₃ groups of the (CNBu-*t*) ligand in Cr(CO)₅(CNBu-*t*). Two other weaker bands in the same region are most probably due to a combination or the first overtone of a lower energy vibrational mode. In the 1400—1200 cm⁻¹ region, the two CH₃ deformation modes could also been monitored for both pressure phases. The ν(CH)ₐₛᵧₘ mode has a much larger pressure dependence than does the ν(CH)ₛᵧₘ mode. The two δ(CH₃) modes behave as typical bending modes in both phases. In the case of *cis*-Cr(CO)₄(CNBu-*t*)₂, the two ν(CH) modes and the CH₃ deformation modes have very low pressure dependences in the low-pressure phase compared to the corresponding values for the monosubstituted complex. In the high-pressure phase, the pressure dependences regain their normal values.