

Pressure-tuning vibrational spectra of the heterobimetallic complexes, $\text{Ph}_3\text{MCo}(\text{CO})_4$ ($\text{M} = \text{Sn}, \text{Pb}$)

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Abstract

Vibrational spectra of two crystalline organometallic complexes of the type, $\text{Ph}_3\text{MCo}(\text{CO})_4$ ($\text{Ph} = \text{C}_6\text{H}_5$; $\text{M} = \text{Sn}, \text{Pb}$), have been recorded at ambient temperature and a range of high pressures up to ~ 56 kbar with the aid of diamond-anvil cells (DACs). The IR and Raman data indicate that the $\text{Sn}^{\text{IV}}\text{-Co}^{\text{I}}$ and $\text{Pb}^{\text{IV}}\text{-Co}^{\text{I}}$ metal–metal bonded complexes undergo structural transformations at around 33 and 24 kbar, respectively. The pressure dependences of the $\nu(\text{Sn-Co})$ and $\nu(\text{Pb-Co})$ modes are comparable in the low-pressure phase (about $0.06 \text{ cm}^{-1} \text{ kbar}^{-1}$), but are quite different in the high-pressure phase (0.37 and $0.08 \text{ cm}^{-1} \text{ kbar}^{-1}$), respectively. The negative pressure dependences of some of the $\nu(\text{CO})$ modes suggest that π -backbonding interactions between the Co atom and the CO groups in both compounds are appreciably strengthened with increasing pressure. Possible reasons for the lower phase-transition pressure for the lead (IV) compound are discussed.

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1. Introduction

The physicochemical properties of organometallic carbonyl complexes have been the subject of almost endless attention over the past 50 years [1] and, during this time, the structural properties of these types of materials have been extensively investigated by a wide array of analytical techniques, including vibrational, e.g. [2–6] and multinuclear NMR spectroscopy, e.g. [7,8], and X-ray [2], electron, e.g. [9,10], and incoherent inelastic neutron scattering diffraction [2]. Of current special interest to our research on organometallic carbonyl complexes are the vibrational spectroscopic properties of metal–metal bonded species of the type, $\text{Ph}_3\text{MCo}(\text{CO})_4$

($\text{M} = \text{Si}, \text{Sn}, \text{Pb}$), which form part of the prototypical class of trigonal–bipyramidal, C_{3v} -symmetry derivatives with the general formula $\text{LCo}(\text{CO})_4$ [11–13]. However, these particular metal–metal bonded complexes exhibit much higher thermal stability when $\text{L} = \text{Ph}_3\text{M}$ ($\text{M} = \text{Si}, \text{Sn}, \text{Pb}$) than when $\text{L} = \text{alkyl}$ or H . It has been suggested that this situation may be attributed to the stronger M-Co π -bonding interactions, because only when L is a π -acceptor ligand are the complexes more thermally stable [13]. Infrared studies of the CO stretching modes and valence force-field calculations for various $\text{LCo}(\text{CO})_4$ complexes have provided evidence for π -interactions in the metal–metal bonds [14–18]. Moreover, the IR and Raman spectra of the closely related complexes, $\text{X}_3\text{MCo}(\text{CO})_4$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), have been examined and vibrational assignments have been proposed [19,20]. The molecular electric dipole moments for a series of $\text{LM}(\text{CO})_4$ complexes, including the

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$\text{Ph}_3\text{MCo}(\text{CO})_4$ ($\text{M} = \text{Si}, \text{Sn}, \text{Pb}$) derivatives, have been reported [21], which indicate that charge-transfer in the $\text{M}-\text{Co}$ bond is mainly determined by the inductive properties of the attached ligands L . The same conclusion was reached for the $\text{Sn}-\text{Fe}$ bond in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{SnPh}_3)$ and related derivatives [22]. More recently, we have published some X-ray diffraction and multinuclear NMR spectroscopic data that have some bearing on the electronic environment and chemical bonding in the $\text{Ph}_3\text{MCo}(\text{CO})_4$ ($\text{M} = \text{Si}, \text{Sn}, \text{Pb}$) derivatives [23].

High-pressure molecular spectroscopic studies on metal-metal bonded species have thus far been focused on homobimetallic complexes, such as the quadrupolar-bonded species $[\text{Re}_2\text{X}_8]^{2-}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) [24,25], $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ [25], and $\text{Re}_2(\text{piv})_4\text{X}_2$ ($\text{piv} = \text{O}_2\text{CCMe}_3$; $\text{X} = \text{Cl}, \text{Br}$) [26] and the metal decacarbonyls $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}, \text{Re}$) [27,28]. Several homopolymetallic clusters, such as $\text{Ru}_3(\text{CO})_{12}$ [29], $[\text{Au}_9(\text{PPh}_3)_8][\text{PF}_6]_3$ [30], $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = 3-5$) [31], and $\text{HOs}_3(\text{CO})_{10}(\mu, \eta^2\text{-NC}_5\text{H}_4)$ [32] have also been examined. We report here the results of a pressure-tuning FT-Raman and IR spectroscopic study of the heterobimetallic complexes Ph_3SnCo

$(\text{CO})_4$ and $\text{Ph}_3\text{PbCo}(\text{CO})_4$. In addition to providing information on the effect of high pressures on the structures of these materials, these high-pressure vibrational measurements afford additional insights into the relative π -backbonding capabilities of the Ph_3M ligands, the nature of the $\text{Sn}-\text{Co}$ and $\text{Pb}-\text{Co}$ bonding, and the charge-transfer effects in the two complexes. This work represents an extension to our earlier studies of the effect of high pressures on the π -backbonding interactions in a wide range of organometallic complexes, including $\text{CH}_3\text{M}(\text{CO})_5$ ($\text{M} = \text{Mn}, \text{Re}$) [33] and Zeise's salt $\text{K}[(\eta^2\text{-C}_2\text{H}_4)\text{PtCl}_3]$ [34].

2. Experimental

2.1. Materials

Octacarbonyldicobalt(0), $\text{Co}_2(\text{CO})_8$, was purchased from Strem Chemical Co; the other reagents used in the preparation of crystalline $\text{Ph}_3\text{MCo}(\text{CO})_4$ ($\text{M} = \text{Sn}, \text{Pb}$) were obtained from Aldrich Chemical Co. All mate-

Table 1
Pressure dependences of observed Raman bands of $\text{Ph}_3\text{SnCo}(\text{CO})_4$

IR (solid)	Raman (solid)			Assignment
	ν (cm^{-1})	Low-pressure phase $d\nu/dP$ ($\text{cm}^{-1} \text{kbar}^{-1}$)	Middle phase $d\nu/dP$ ($\text{cm}^{-1} \text{kbar}^{-1}$)	
	84 vs	0.06		e $\delta(\text{SnCoC})$
	109 vs	0.13		e $\delta(\text{PhSnCo})$
	150 w			a_1 $\delta(\text{CCoC})$
	171 s	0.05	0.82	a_1 $\nu(\text{Sn}-\text{Co})$
	212 m	0.31		e $\delta(\text{SnPh}_3)$
	237 w			
	264 w			
	372 w			
424 w	422 m	0.07	0.80	a_1 $\nu(\text{Co}-\text{CO})$
447 w	446 w			
493 sp	490 w			
513 sp	514 w			
547 w	548 w			
616 w	616 w			
658 w	655 m	0.12	0.31	0.33
698 m	698 w			
728 m	730 w			
	1989 m	-0.15	-0.30	e' $\nu(\text{CO})$
1997 s	2001 m	-0.14	-0.26	e $\nu(\text{CO})$
2026 m	2030 s	0.06	0.21	a_1^{ax} $\nu(\text{CO})$
2087 m	2087 m	0.04	0.52	a_1^{eq} $\nu(\text{CO})$
2951 w	2951 w			$\nu(\text{CH})$
2988 w	2990 w			$\nu(\text{CH})$
3014 m	3014 w			$\nu(\text{CH})$
	3042 m	0.05	1.47	$\nu(\text{CH})$
3049 m	3048 m	0.05	1.30	$\nu(\text{CH})$
3067 m	3068 w			$\nu(\text{CH})$
3136 w	3137 w			$\nu(\text{CH})$
	3152 w			$\nu(\text{CH})$

rials were used as received. With the exception of THF (which was dried over Na metal using benzophenone indicator), the solvents were not dried before use. All synthetic reactions were performed under a dry-N₂ atmosphere, with subsequent work-up being under air, as described earlier by Darensbourg [35].

2.2. High-pressure vibrational spectroscopic measurements

Infrared spectra were recorded at 1.0-cm⁻¹ resolution in the 4000–400 cm⁻¹ range at ambient temperature and various selected pressures, using a Bruker IFS-48 spectrometer coupled to a Bruker 8590 microscope and a Sony colour video system, equipped with a liquid N₂-cooled MCT-D326 detector. A diamond-anvil cell (DAC, High Pressure Diamond Optics, Tucson, Arizona), fitted with a pair of type-IIA diamonds, was used to produce the high pressures and the shift of the anti-symmetric N–O stretching mode of dry NaNO₂ (~3%) in NaBr, originally located at 1401.6 cm⁻¹, was employed as the internal pressure calibrant [36]. The samples and the pressure calibrant were placed, with the aid of a standard optical microscope, into a 300-μm

diameter hole drilled in the center of a 3-mm square, 300-μm thick, stainless-steel gasket. The gasket was necessary to ensure that the pressure gradient over the diamond faces was minimal since no pressure-transmitting fluid was deemed necessary for the pressure range being investigated.

FT-Raman spectra were measured at ambient temperature and high pressures in the 0–4000 cm⁻¹ range on a Bruker IFS-88 spectrometer coupled to FRA-106 FT-Raman module, using a Nd³⁺:YAG laser with an excitation line at 1064.1 nm, equipped with a proprietary liquid N₂-cooled Ge detector. The same DAC and sampling technique that was used for the pressure-tuning IR measurements was also used for the pressure-tuning Raman work, except that the phonon band associated with the 1332.5 cm⁻¹ band of the type-II diamonds themselves in the DAC was employed as an in situ, internal pressure calibrant [37].

The high-pressure measurements were repeated twice for each complex to ensure the validity of the observed pressure-induced behavior of the vibrational bands and their measured pressure dependences. Because it was impossible to generate identical pressures manually when using the DAC, however, only the results from

Table 2
Pressure dependences of observed Raman bands of Ph₃PbCo(CO)₄

IR (solid)	Raman (solid)			Assignment
	ν (cm ⁻¹)	Low-pressure phase $d\nu/dP$ (cm ⁻¹ kbar ⁻¹)	Middle phase $d\nu/dP$ (cm ⁻¹ kbar ⁻¹)	
	82 s	0.05		<i>e</i> δ(SnCoC)
	107 vs	0.08		<i>e</i> δ(PhSnCo)
	155 s	0.07	0.84	<i>a</i> ₁ ν(Pb–Co)
	202 s	0.05		
	220 w			<i>e</i> δ(SnPh ₃)
	255 w			
	370 w			
420 w	418 m	0.10	0.85	<i>a</i> ₁ ν(Co–CO)
444 w	440 w			
490 sp	487 w			
503 sp	502 w			
544 w	545 w			
614 w	614 w			
646 w	645 m	0.08	0.22	0.09
696 m	696 w			
730 m	729 w			
	1988 m	–0.06	–0.20	<i>e'</i> ν(CO)
1995 s	1997 m	0.04	0.09	<i>e</i> ν(CO)
2020 m	2023 s	0.03	0.78	<i>a</i> ₁ ^{ax} ν(CO)
2080 m	2080 m		0.42	<i>a</i> ₁ ^{eq} ν(CO)
2957 w	2858 w			ν(CH)
2985 w	2887 w			ν(CH)
3014 m	2941 w			ν(CH)
	3031 m			ν(CH)
3040 m	3040 m			ν(CH)
3066 m	3066 w			ν(CH)
3136 w	3137 w			ν(CH)
	3152 w			

one set of IR and Raman measurements are reported for each complex. The band positions given in Tables 1 and 2 are considered to be accurate to within $\pm 1.0 \text{ cm}^{-1}$ and were determined using the Bruker OPUS software. The pressures reported are generally considered to be accurate to better than $\pm 0.5 \text{ kbar}$, while the uncertainty in the actual phase transition pressures reported is about $\pm 1.0 \text{ kbar}$.

3. Results and discussion

The behaviour under pressure of some selected Raman bands of $\text{Ph}_3\text{SnCo}(\text{CO})_4$ and $\text{Ph}_3\text{PbCo}(\text{CO})_4$ are shown in Figs. 1 and 2, respectively. Assignments for the vibrational modes are indicated in Tables 1 and 2; these assignments are based on those reported previously for the related $\text{X}_3\text{SnCo}(\text{CO})_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) complexes [19,20]. Assuming C_{3v} symmetry for the two $\text{Ph}_3\text{MCo}(\text{CO})_4$ molecules and treating the Ph groups as point masses leads [38,39] to the following vibrational

representation and spectroscopic activity: $\Gamma_{\text{vib}} = 9a_1(\text{IR,R}) + 2a_2(\text{inact.}) + 11e(\text{IR,R})$.

The low-energy Raman bands observed for $\text{Ph}_3\text{SnCo}(\text{CO})_4$ at 237, 212, 171, 109 and 84 cm^{-1} are assigned, respectively, as the $e \delta(\text{SnPh}_3)$, $a_1 \delta(\text{CCoC})$, $a_1 \nu(\text{Sn-Co})$, $e \delta(\text{PhSnCo})$ and $a_1 \delta(\text{SnCoC})$ modes. These modes exhibit small pressure dependences at low pressures, but undergo significant changes in band positions, intensities and widths in the 29.0–38.5 kbar pressure region. Discontinuities also occur in the pressure vs. wavenumber plots for the analogous lead (IV) compound and so it appears that there are pressure-driven structural transformations at $\sim 33 \text{ kbar}$ for $\text{Ph}_3\text{SnCo}(\text{CO})_4$ and $\sim 24 \text{ kbar}$ for $\text{Ph}_3\text{PbCo}(\text{CO})_4$. Lattice vibrational modes are particularly sensitive to changes in the packing of molecules in the unit cells of crystalline materials, e.g., the pressure-induced phase transitions that occur in certain ferroelectric materials are driven by the lowest energy phonon soft modes [40]. No such phonon soft modes were observed, however, for the lattice region of the two compounds studied in this work. The pressure dependences of the $\nu(\text{Sn-Co})$ and $\nu(\text{Pb-Co})$ modes in the low-pressure phases are quite similar, viz., 0.05 and $0.07 \text{ cm}^{-1} \text{ kbar}^{-1}$, respectively. Following the phase transition, however, the pressure dependence for the $\nu(\text{Sn-Co})$ mode becomes strikingly different ($0.37 \text{ cm}^{-1} \text{ kbar}^{-1}$), while that for the $\nu(\text{Pb-Co})$ mode is essentially unchanged ($0.08 \text{ cm}^{-1} \text{ kbar}^{-1}$).

Figs. 1(a) and (b) illustrate how the vibrational modes originally located at 109 and 84 cm^{-1} for $\text{Ph}_3\text{SnCo}(\text{CO})_4$ and at 155, 107 and 82 cm^{-1} for $\text{Ph}_3\text{PbCo}(\text{CO})_4$ develop into broad bands centered at 150 and 148 cm^{-1} at pressures of 32.5 and 28.5 kbar, respectively. Pressure broadening is also observed for other Raman modes, e.g., the $a_1 \nu(\text{Co-Sn})$ mode of $\text{Ph}_3\text{SnCo}(\text{CO})_4$ at 171 cm^{-1} (Fig. 3). The broadness of Raman bands with increasing pressure is may be partly the result of non-hydrostatic gradients across the faces of the diamonds in the DAC.

The assignments given for the Raman-active $\nu(\text{CO})$ modes for $\text{Ph}_3\text{SnCo}(\text{CO})_4$ are 2087 [a_1^{eq}], 2030 [a_1^{ax}] and $2001 (e) \text{ cm}^{-1}$. There is an additional peak at 1989 cm^{-1} , denoted as the $e' \nu(\text{CO})$ mode, which results from splitting of the $e \nu(\text{CO})$ mode because the threefold symmetry is actually lowered by the presence of the three Ph groups on the Ph_3Sn ligand. Upon going from ambient pressure to $\sim 33 \text{ kbar}$, the pressure-tuning data indicate that the $a_1^{\text{eq}} \nu(\text{CO})$ mode displays a slight positive pressure dependence ($0.04 \text{ cm}^{-1} \text{ kbar}^{-1}$), while the $e \nu(\text{CO})$ and $e' \nu(\text{CO})$ modes exhibit negative pressure dependences of -0.14 and $-0.15 \text{ cm}^{-1} \text{ kbar}^{-1}$, respectively. In the high-pressure phase, all the bands shift towards higher energies, as is typically the case [41]. For the related $\text{Ph}_3\text{PbCo}(\text{CO})_4$ complex, the $e' \nu(\text{CO})$ mode at 1988 cm^{-1} shows a slight negative pressure dependence ($-0.06 \text{ cm}^{-1} \text{ kbar}^{-1}$), but the two $\nu(\text{CO})$ modes

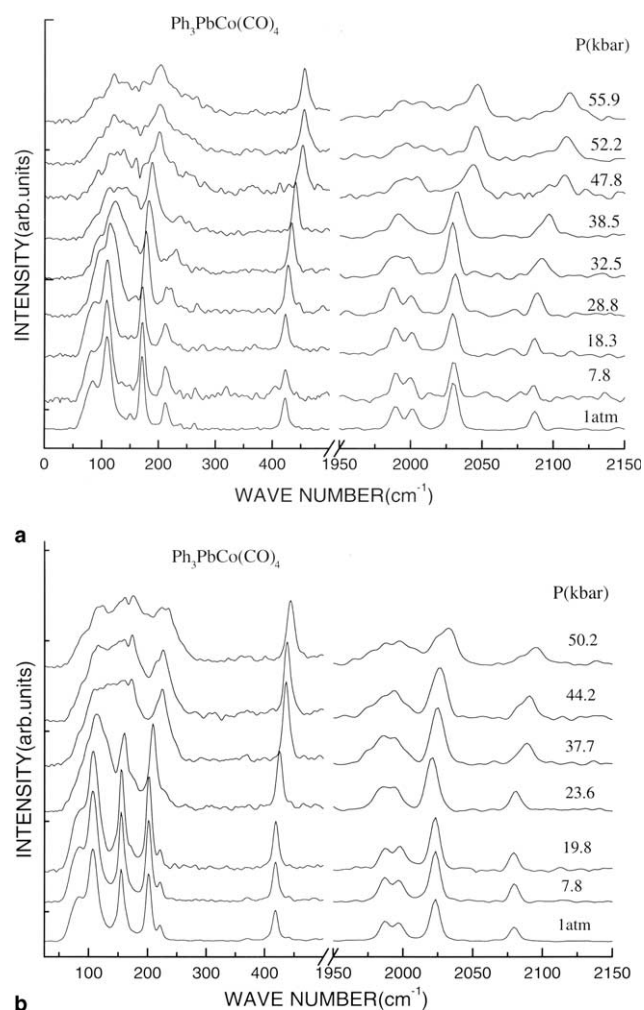


Fig. 1. Raman spectra at various pressures for (a) $\text{Ph}_3\text{SnCo}(\text{CO})_4$ and (b) $\text{Ph}_3\text{PbCo}(\text{CO})_4$.

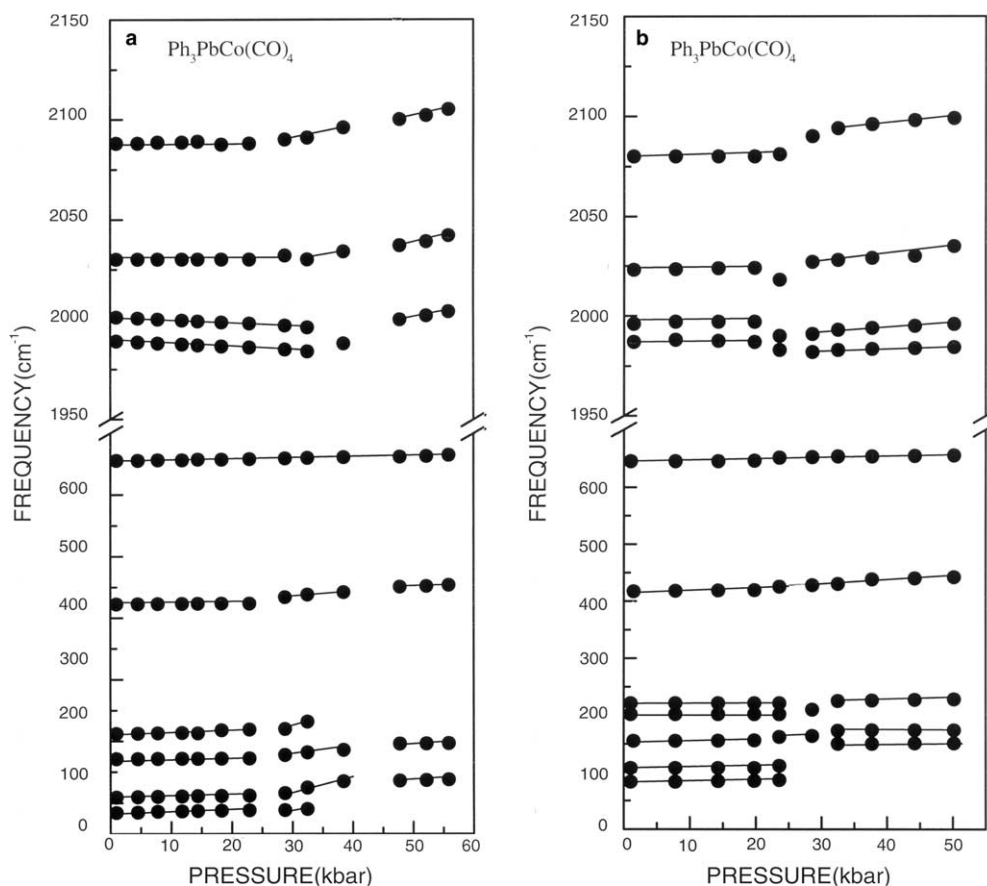


Fig. 2. Pressure dependence of selected Raman-active modes for (a) $\text{Ph}_3\text{SnCo}(\text{CO})_4$ and (b) $\text{Ph}_3\text{PbCo}(\text{CO})_4$.

at 2080 (a_1^{eq}) and 2023 (a_1^{ax}) cm^{-1} and the $e \nu(\text{CO})$ mode at 1997 cm^{-1} are almost independent of pressure up to ~ 20 kbar.

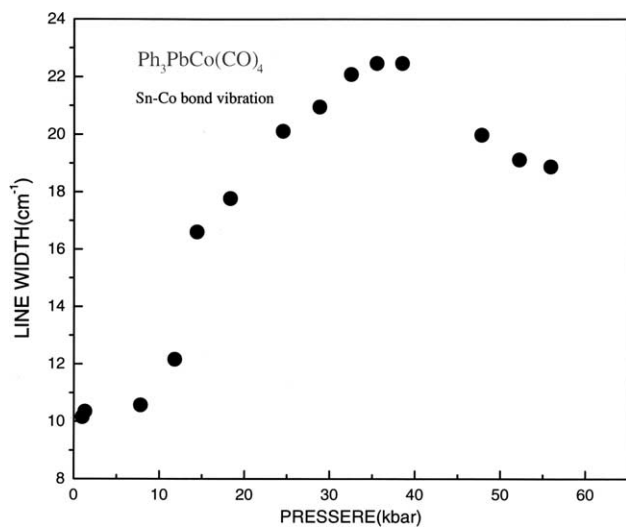


Fig. 3. Pressure dependence of the line-width of the Raman-active $\nu(\text{Sn-Co})$ mode of $\text{Ph}_3\text{SnCo}(\text{CO})_4$.

The differences in the pressure sensitivities of the $\nu(\text{M-Co})$ ($\text{M} = \text{Sn}, \text{Pb}$) and $\nu(\text{CO})$ modes in the two metal-metal bonded complexes are most probably related to differences in the *trans*-effects of the two Ph_3M ligands. The charge transfer in the M-Co bond is determined chiefly by the inductive properties of the groups attached to M [21,22]. The *trans*-effect is the net result of the opposing π -acceptor and σ -donor effects [3]. The inductive Ph_3Sn and Ph_3Pb ligands have comparable π -acceptor/ σ -donor parameters of $-0.59/0.41$ and $-0.60/0.42$, respectively, indicating that the σ -donor capacities of both ligands are greater than are their π -acceptor capacities [42]. Since some of the $\nu(\text{CO})$ modes exhibit negative pressure dependences, it appears that the CO groups in the $\text{Co}(\text{CO})_4$ moiety are attracting more electron density from the filled $\text{Co } 3d_\pi$ orbitals than do the Ph_3M ligands and that this electron density goes into the π^* - CO orbitals, thereby resulting in a decrease in energy in some of the $\nu(\text{CO})$ modes [42]. These π -backbonding effects are apparently sufficient to override the normal effect of pressure, which is to increase the vibrational energies [41]. Similar negative $\nu(\text{CO})$ and $\nu(\text{C=C})$ pressure dependences have been observed for several other organometallic complexes, including

$\text{CH}_3\text{M}(\text{CO})_5$ ($\text{M} = \text{Mn}, \text{Re}$) [33], $\text{K}[(\eta^2\text{-C}_2\text{H}_4)\text{PtCl}_3]$ [34] and $\text{Mn}(\text{CO})_5\text{Br}$ [43].

The phenyl groups on the Ph_3M ligands may undergo changes in torsional angles as the packing forces increase due to the contraction of the unit cells under compression. At ambient pressure, the Sn–Co and Pb–Co bond lengths in the two $\text{Ph}_3\text{MCo}(\text{CO})_4$ complexes are 2.5953 and 2.667 Å, respectively, while the unit cell volumes are 1087.92 and 1077.6 Å³, respectively [23]. Therefore, even at ambient pressure, the lead (IV) complex is already slightly more “compressed” than is the tin (IV) analogue and this may be partly why the phase transition in this complex occurs at a lower pressure (23.5 vs. 32.5 kbar). In addition, the larger size of the lead atom compared to tin may also play a role in this difference because the lattice contractions in the lead complex will result in stronger π -interactions with the $\text{Co}(\text{CO})_4$ moiety than will those in the tin complex.

The Raman bands at 425 and 418 cm^{-1} for $\text{Ph}_3\text{SnCo}(\text{CO})_4$ and $\text{Ph}_3\text{PbCo}(\text{CO})_4$, respectively, are assigned to the a_1 $\nu(\text{Co-CO})$ mode in each case. Fig. 4 compares the pressure dependence of the intensity of the a_1 $\nu(\text{Co-CO})$ mode for the tin complex with that of the e $\nu(\text{CO})$ mode. The a_1 $\nu(\text{Co-CO})$ mode exhibits a marked increase in intensity with increasing pressure, which reaches a maximum in the phase-transition region. Similarly, the pressure dependence of the intensity of the a_1 $\nu(\text{Co-CO})$ mode for the tin complex is much greater than for the lattice modes at 109 and 84 cm^{-1} (Fig. 1(a)). Similar dependences of band intensities on pressure are also observed for $\text{Ph}_3\text{PbCo}(\text{CO})_4$

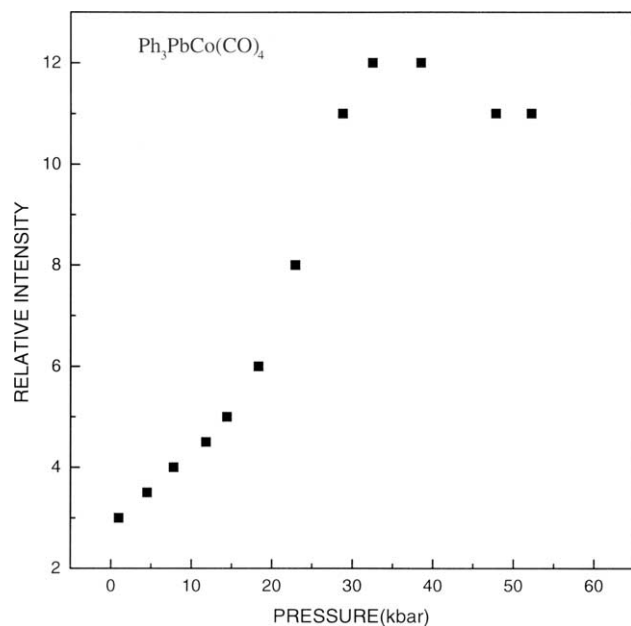


Fig. 4. Pressure dependence of the relative intensity of Raman-active a_1^{ax} $\nu(\text{Co-CO})$ mode of $\text{Ph}_3\text{SnCo}(\text{CO})_4$.

(Fig. 1(b)). These interesting changes in Raman band intensities presumably result chiefly from charge-transfer effects in the $\text{Ph}_3\text{MCo}(\text{CO})_4$ systems. The effects of charge transfer on Raman intensities can be predicted by Raman intensity theory in which it has been shown that the contribution to the Raman intensity of a totally symmetric vibration is closely related to a particular intermediate electronic excited state [44]. For example, the effects of hydrogen bonding on the Raman intensities of methanol, ethanol and water have been studied and it was concluded that the intensity changes observed are due to the additional contribution of the charge-transfer electronic excited state arising from hydrogen bond formation [45].

At ambient pressure, the Raman spectra in the 3200–2950 cm^{-1} region reveal several features for the tin compound, but only the $\nu(\text{CH})$ bands at 3048 and 3042 cm^{-1} bands are strong enough to be detected at higher pressures. The pressure dependences of these two $\nu(\text{CH})$ bands are illustrated in Fig. 5; both modes display very small, positive shifts in the low-pressure phase, but much larger shifts towards higher wavenumbers on going from 29.0 to 38.5 kbar with pressure sensitivities of 1.30 and 1.47 $\text{cm}^{-1}\text{kbar}^{-1}$, respectively, during the transition. At higher pressures, the pressure sensitivities are quite normal ($\sim 0.50 \text{ cm}^{-1}\text{kbar}^{-1}$) [37]. Broadening of the two bands can also be clearly seen and, following the structural transition, the bands

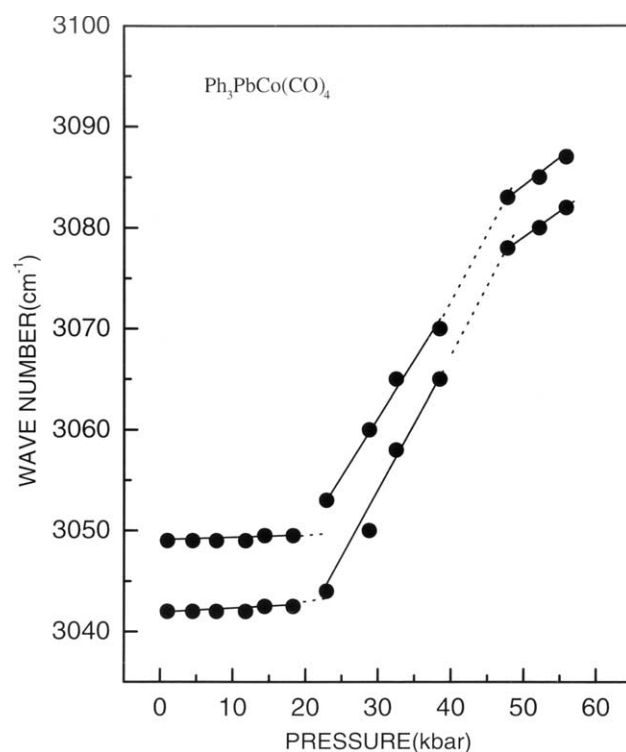


Fig. 5. Pressure dependences of Raman-active $\nu(\text{CH})$ modes for $\text{Ph}_3\text{SnCo}(\text{CO})_4$.

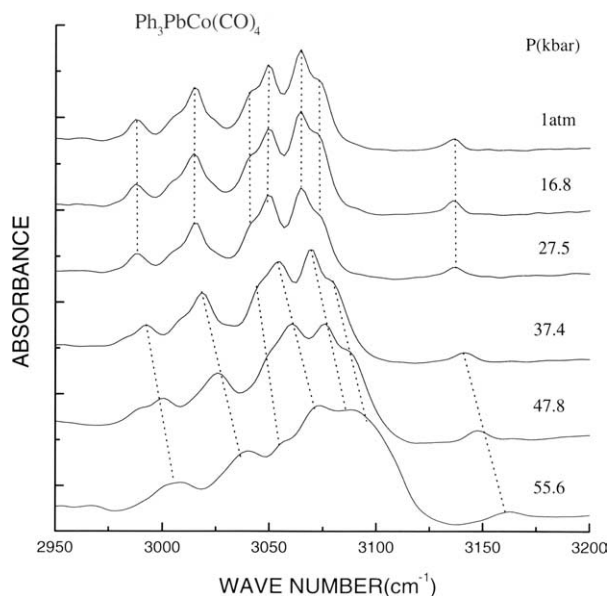


Fig. 6. IR spectra of $\nu(\text{CH})$ modes for $\text{Ph}_3\text{SnCo}(\text{CO})_4$ at various pressures.

begin to show slight increases in energy with increasing pressure.

Despite the fact that $\nu(\text{CO})$ modes are buried beneath the intense IR absorption near 2000 cm^{-1} from the diamonds in the DAC, it is still possible to extract some useful information from the pressure-tuning IR measurements. Several $\nu(\text{CH})$ bands were detected at ambient temperature and various pressures, e.g., see Fig. 6 for the case of $\text{Ph}_3\text{SnCo}(\text{CO})_4$. These bands shift towards high energies in the pressure range studied, especially in the 27.5–37.5 kbar region. Discontinuities in the pressure vs. wavenumber plots for all of these bands are detected at ~ 38 kbar, providing additional support to the conclusion from the Raman measurements on this compound that there is a structural transformation occurring in the neighbourhood of 30 kbar. Moreover, when the external pressure reaches 55.5 kbar, the IR-active $\nu(\text{CH})$ peaks develop into a broad band. These pressure dependences of the $\nu(\text{CH})$ bands in the IR are similar to those obtained in the Raman work. More detailed studies on the effects of high pressures on the $\nu(\text{CH})$ bands of some pure hydrocarbons have been reported, e.g., quadricyclane [46] and norbornylene [47].

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