TABLE II

ENTHALPIES AND ENTROPIES OF TRANSITION AND FUSION FOR SEVERAL ORGANOSILICON COMPOUNDS

	Transition		Fusion	
	ΔH, cal/g	ΔS, eu	ΔH, cal/g	ΔS, eu
Tetrakis(trimethylsilyl)silane	8.62	11.5	...	...
Tris(trimethylsilyl)amine	8.08	7.7	1.81	1.3
N,*N'*-Bis(trimethylsilyl)tetramethylcyclodisilazane	...	...	18.93	17.6
Hexamethylcyclotrisiloxane	...	...	21.59	14.4

methylsilyl)silane indicate that not much greater overall conformational freedom is acquired than in the transition for hexamethyldisilane (10.5 eu). For comparison, thermal data for the fusion of two substances not exhibiting a mesocrystalline phase are also reported.

Experimental Section

All qualitative data were determined with a Du Pont differential thermal analyzer at a heating rate of 15°/min in an air atmosphere. The quantitative data were obtained with the differential scanning calorimeter module at a heating rate of 10°/min. The procedure and calibration were described earlier.[11] Tetrakis(trimethylsilyl)silane was prepared by Gilman's procedure[1] and tris(trimethylsilyl)amine by Lehn's procedure.[12] The synthesis of *N*,*N'*-bis(trimethylsilyl)tetramethylcyclodisilazane[13] as well as bis(chlorodimethylsilyl)trimethylsilylamine and bis(dimethylamino)dimethylsilylamine[6] has been described elsewhere. Tris(chlorodimethylsilyl)amine was prepared by Wannagat's procedure[14] and had the following elemental analyses. *Anal.* Calcd for $C_6H_{18}Cl_3NSi_3$: C, 24.44; H, 6.15; Cl, 36.08; N, 4.75; Si, 28.58. Found: C, 24.62; H, 6.31; Cl, 36.10; N, 4.81; Si, 28.30.

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Raman Intensities and Bond Orders in the Hexacarbonyls of Chromium, Molybdenum, and Tungsten[1]

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Few questions have interested inorganic chemists more than the extent of π back-bonding from metal to ligand in the transition metal carbonyls and their derivatives. As the most symmetric representatives of this class of molecules, the group IV hexacarbonyls have attracted particular attention. Recently Jones, *et al.*,[2] carried out a very thorough analysis of the vibrational spectra of these molecules, including $^{12}C^{18}O$ and $^{13}C^{16}O$ isotopes, and determined accurate force constants. The order of the primary metal–carbon stretching constants and by implication that of the M–C bond strengths is W > Cr $\gtrsim$ Mo. This order is reproduced in estimates of M–C bond energies from kinetic[3] and photoionization[4] data. It has been suggested[4] that the origin for this order lies in an irregular variation of valence orbital ionization potentials for the metal atoms. Molecular orbital calculations support the impression of extensive donation of metal electrons to the π^* carbonyl orbitals.[5–7]

Absolute Raman intensities offer the promise of an independent estimate of π bonding. From the intensities of totally symmetric modes one can obtain bond polarizability derivatives by a well-defined transformation.[8] It has long been recognized that these derivatives are related to covalency, and they have been interpreted as reflecting the extent of π bonding in various molecules.[9,10] Recently Long and Plane proposed an equation that relates bond polarizability derivatives directly to bond order.[11] While the theoretical basis for the equation is very approximate, it has proved quite successful in predicting polarizability derivatives for a variety of well-characterized molecules.

The group VI hexacarbonyls provide a particularly opportune subject for a Raman intensity study. Because of their high symmetry, the only internal coordinates that contribute to totally symmetric modes are the two of interest here: M–C and C–O stretching. The problem of coordinate mixing is therefore reduced to a minimum. Furthermore the degree of mixing for the two coordinates can be evaluated with considerable confidence, thanks to the accurate force constants calculated by Jones, *et al.*[2]

Experimental Section

The laser Raman spectrometer and its intensity calibration have been described elsewhere.[12] The 6471-Å line of the Ar–Kr laser was used for excitation. The hexacarbonyls were obtained from Alfa Inorganics. Raman intensities for the A_{1g} modes were measured in CCl_4 solution for $Cr(CO)_6$ and $Mo(CO)_6$ and in CS_2 solution for $W(CO)_6$. Concentrations ranged from 0.01 to 0.07 *M*. The intensities were corrected for instrument response and converted to normal mode polarizability derivatives, $\bar{\alpha}'_Q$, with the equation[8]

$$I_Q = \frac{KM(\nu_0 - \Delta\nu)^4}{\Delta\nu[1 - \exp(-h\Delta\nu/kT)]}\left[45\left(\frac{6}{6 - 7\rho}\right)\bar{\alpha}'_Q{}^2\right] \quad (1)$$

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Table I

Raman Intensity Results

Molecule	Internal coordinate	ν_{A1g}, cm^{-1}	R^a	$\bar{\alpha}'_Q$,[b] Å/amu$^{1/2}$	$\bar{\alpha}'_u$,[c] Å^2 Set 1	$\bar{\alpha}'_u$,[c] Å^2 Set 2	$n/2$[d] Set 1	$n/2$[d] Set 2	Valence force constant,[e] mdyn/Å	Bond distance,[f] Å
$Cr(CO)_6$	M–C	381	3.06	1.05	2.15	2.39	1.62	1.82	2.10	1.916
	C–O	2112	0.77	1.74	3.13	−0.45	4.36	−0.63	17.04	1.171
$Mo(CO)_6$	M–C	402	3.76	1.21	2.53	2.73	1.27	1.37	2.00	2.063
	C–O	2117	0.53	1.44	3.04	0.06	4.58	0.09	17.15	1.145
$W(CO)_6$	M–C	427	5.04	1.54	3.25	3.41	1.80	1.89	2.32	2.058
	C–O	2117	0.22	0.92	2.91	1.04	4.38	1.57	17.02	1.148

[a] Molar intensity of the indicated band relative to the molar intensity of the ν_1 line of CCl_4, corrected for spectrometer sensitivity. The estimated uncertainties are 10–15%. [b] Polarizability derivative for the indicated normal mode. [c] Bond polarizability derivatives obtained with eq 2. The signs of $\bar{\alpha}'_{Q_{M-C}}$ and $\bar{\alpha}'_{Q_{C-O}}$ were taken as +, + for set 1 and +, − for set 2. [d] Calculated using eq 3, with the following parameters: $Z_M = 6, Z_C = 4, Z_O = 6$; $X_{Cr} = 1.6, X_{Mo} = 1.8, X_W = 1.7, X_C = 3.3, X_O = 3.0$. Bond distances are given in the last column. [e] Reference 2. [f] A. Whitaker and J. W. Jeffrey, *Acta Crystallogr.*, **23**, 977 (1967); S. P. Arnesen and H. M. Seip, *Acta Chem. Scand.*, **20**, 2711 (1966).

Here K is an instrumental constant, M is the molar concentration, ν_0 is the exciting frequency, $\Delta\nu$ is the Raman shift, and ρ is the depolarization ratio. For totally symmetric modes of isotropic molecules, $\rho = 0$. The intensities were placed on an absolute scale by comparison with the intensity of the ν_1 line of CCl_4, for which $\bar{\alpha}'_Q = 0.686$ Å^2 amu$^{-1/2}$.[11] For $W(CO)_6$ the intensities were compared with the ν_1 line of CS_2, which in turn was compared with ν_1 of CCl_4 in a 50:50 (v/v) mixture of the two solvents.

Results

Intensities and normal mode polarizability derivatives for the hexacarbonyls are given in Table I. Bond polarizability derivatives, $\bar{\alpha}'_{u_j} \equiv \partial\bar{\alpha}/\partial u_j$, where u_j is an internal coordinate of the jth set, can be calculated *via* the transformation[8]

$$\bar{\alpha}'_{Q_p} = \sum_j \sqrt{N_j}\, l_{jp}\bar{\alpha}'_u \qquad (2)$$

where N_j is the number of internal coordinates in the symmetry coordinate S_j, and l_{jp} is the eigenvector element connecting S_j with the normal coordinate Q_p. The eigenvectors, calculated[13] with the aid of the force constants given by Jones, *et al.*,[2] are given in Table II.

Table II

Eigenvector Elements for A_{1g} Modes of $M(CO)_6$

	$Cr(CO)_6$ Q_{CO}[a]	$Cr(CO)_6$ Q_{MC}	$Mo(CO)_6$ Q_{CO}	$Mo(CO)_6$ Q_{MC}	$W(CO)_6$ Q_{CO}	$W(CO)_6$ Q_{MC}
S_{CO}[b]	0.38160	0.01272	0.38151	0.01443	0.38147	0.01563
S_{MC}	−0.22424	0.18137	−0.22413	0.18056	−0.22612	0.17957

[a] Q_{CO} and Q_{MC} are the A_{1g} normal modes that involve primarily C–O and M–C stretching, respectively (frequencies given in Table I). [b] Symmetry coordinates: $S_{CO} = (1/\sqrt{6})\Sigma_N{}^6\Delta(CO)_N$; $S_{MC} = (1/\sqrt{6})\Sigma_N{}^6\Delta(MC)_N$.

Unfortunately there is a sign ambiguity in eq 2 because Raman intensity is proportional to the *square* of $\bar{\alpha}'_Q$ (eq 1). If there is only one term in the summation or if all terms but one are negligible (no mixing), the result is simply a sign ambiguity in the calculated bond polarizability derivative. However, if two terms are important, then there is an ambiguity as well in the magnitude of the two $\bar{\alpha}'_u$'s since $\bar{\alpha}'_{Q_1}$ and $\bar{\alpha}'_{Q_2}$ can be taken with the same or different signs. There are four possible combinations of signs for the $\bar{\alpha}'_Q$'s and two pairs of solutions to the two simultaneous equations, the pairs differing only in sign. This is the situation in the present study, and Table I lists the more positive pair of values of $\bar{\alpha}'_u$ for each molecule. Table I also lists estimates of bond orders obtained from the bond polarizability derivatives, *via* the Long and Plane equation[11]

$$n/2 = \frac{3}{2}\frac{Za_0}{g\sigma}\frac{\bar{\alpha}'_u}{r^3}$$

where n is the number of electrons in the bond, a_0 is the Bohr radius, r is the bond distance, σ is the Pauling covalent bond character, Z is the effective nuclear charge (taken as the atomic number minus the number of inner shell electrons), and g is the δ function strength (taken as the square root of the Pauling electronegativity) for the atoms forming the bond. For heteronuclear bonds the geometric mean of Z/g is taken. We used sp valence state electronegativities for C and O, as given by Hinze and Jaffé,[14] a procedure which gives a reasonable result for acetylene.[11]

A glance at Table I shows that the results for the C–O bond are disappointing. Whereas a bond order between 2 and 3 is expected, we are left with a choice, depending on which signs are accepted for the $\bar{\alpha}'_Q$'s, between a set of C–O bond orders between 4.2 and 4.4, or another set which varies from 1.5 to −0.6. Inasmuch as the C–O force constants are essentially constant, the former set may be taken as preferable (in fact the slight variations in bond order parallel those in the force constants), but it is nevertheless hardly satisfactory in absolute magnitude. A similar situation was encountered by Chantry and Plane[15] in a study of transition metal cyanide complexes. The C–N bond polarizability derivative came out much higher in the complexes than in free cyanide ion or in acetonitrile. They attributed this anomaly to a breakdown in the basic assumption of bond polarizability theory, namely, that molecular polarizability derivatives are the sums of contributions from individual bonds.

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Cyanide and carbonyl complexes in which π back-bonding is important are indeed precisely where this assumption might be expected to break down. The extent of π overlap between M and C and between C and O (or N) are interrelated and depend sensitively on the nuclear coordinates. Table II shows that the eigenvectors for the high-frequency "C–O stretching" mode actually contain a $\sim$35% negative contribution from the M–C stretching coordinate. This seems surprising since we are accustomed to thinking of the C–O stretching modes as quite pure, and indeed they are pure from the point of view of the potential energy distribution,[2] in which the eigenvector elements are weighted by the force constants. It is characteristic of linear systems of this kind, however (see for example the thiocyanate ion[16]), that the higher frequency mode is badly mixed with respect to the eigenvector elements themselves. In other words, as the C–O bonds are stretched, in the high frequency A_{1g} mode, the M–C bonds are substantially compressed. The result should be a significant transfer of π overlap from C–O to M–C and a concomitant change in the molecular polarizability, which is not allowed for in bond polarizability theory. This synergistic effect could account for unreasonably high $\bar{\alpha}'_{CO}$ and $\bar{\alpha}'_{CN}$ values.

On the other hand, the eigenvectors for the M–C modes are quite pure. Table II shows that the contributions from C–O stretching are only about 8%, and they are positive (M–C and C–O bonds are stretched in phase). We might therefore hope that π-overlap synergism is slight for these modes. Table I shows that the M–C bond order estimates are indeed quite reasonable. While they exceed the theoretical maximum,[17] 1.5, for Cr–C and W–C, the discrepancies are within the error limits of the Long and Plane equation.[11] Furthermore, because the eigenvectors are nearly pure, the $\bar{\alpha}'_{M-C}$ magnitudes are substantially independent of the choice of sign for the $\bar{\alpha}'_Q$'s, and there is little to choose between the values in set 1 and set 2.

Significantly, the M–C bond order estimates fall in the same order, $W > Cr \gtrsim Mo$, as do the M–C stretching force constants, strengthening the inference that this is also the order of decreasing π back-bonding. It should be noted that the bond polarizability derivatives themselves do not have the same order. They fall into line when reduced to $n/2$ values because of the differences in the M–C bond distances and the importance of the r^3 term in the Long and Plane equation.

We conclude that the Raman intensity data support the well-accepted notion that π back-bonding is significant in the group VI hexacarbonyls, as well as the impression gained from the best force constants available and from bond energy estimates that the extent of such bonding decreases in the order $W > Cr \gtrsim Mo$. On the other hand the data give inflated results with regard to the C–O bonds, probably because of synergistic effects which are neglected in bond polarizability theory.

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The Preparation and Properties of Lithium Bis(borane)dimethylphosphide(1−)

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In 1955 Schaeffer and Basile[1] reported that the reaction of diborane with lithium amide in diethyl ether yields only aminoborane polymer and lithium borohydride

$$LiNH_2 + B_2H_6 \longrightarrow LiBH_4 + (NH_2BH_2)_x \qquad (1)$$

We have found that, unlike lithium amide, lithium dimethylphosphide reacts with diborane in ether solvents to produce lithium bis(borane)dimethylphosphide(1−) (I)

$$Li(CH_3)_2P + B_2H_6 \longrightarrow Li(CH_3)_2P(BH_3)_2 \qquad (2)$$

This paper reports the preparation, properties, and some of the reactions of I.

Experimental Section

General Data.—Reactions were carried out with the aid of a standard high-vacuum system. Air-sensitive materials were manipulated in nitrogen-filled drybags or in the vacuum line. Diethyl ether, monoglyme (1,2-dimethoxyethane), and dioxane were stored in evacuated bulbs over lithium aluminum hydride and, when needed, were condensed directly into the reaction vessel. Boron-11 nmr spectra were obtained using a Varian HA-100 spectrometer operating at 32.1 MHz; proton nmr spectra were obtained with Varian HA-100 and A-60 instruments. Boron-11 and proton chemical shifts are in ppm relative to diethyl ether–boron trifluoride and tetramethylsilane (TMS), respectively. Infrared spectra were obtained using Perkin-Elmer 137 and 337 spectrophotometers.

Reagents.—Diborane and B_2D_6 were prepared by the reaction of polyphosphoric acid with sodium borohydride and $NaBD_4$, respectively. Phenyllithium was prepared in diethyl ether from bromobenzene and lithium wire containing 1% sodium (Alfa Inorganics, Inc.) by the method of Gilman and Morton.[2] Dimethylphosphine was prepared from the reaction of tetramethyldiphosphine disulfide with lithium aluminum hydride in dioxane.[3] Lithium dimethylphosphide was prepared from phenyllithium and dimethylphosphine in diethyl ether.[4]

Reaction of $LiP(CH_3)_2$ with B_2H_6.—In a typical reaction, a 200-ml reaction vessel was charged with 2.69 mmol (determined from dimethylphosphine consumption) of lithium dimethylphosphide in 5 ml of monoglyme. A 3.10-mmol sample of diborane was condensed into the evacuated vessel, which was then warmed to room temperature and stirred magnetically for 1 hr. Separation of the volatile products produced only monoglyme and 0.32 mmol of diborane, implying a 2.78 mmol consumption of diborane. The involatile residue consisted of a viscous oil which, after treatment with 5 ml of anhydrous dioxane and evaporation of the solution under vacuum, yielded a colorless crystalline solid which was then washed with heptane and cold dioxane and dried under vacuum.

Analysis of the compound presented a problem because the material contained an appreciable, though evidently nonstoichiometric, quantity of lithium bromide[5] introduced from the phenyl-

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