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Charged Carbonyls in Matrices. An Infrared Structural Characterization of Ni(CO)$_3^-$, Cr(CO)$_5^-$, and Fe(CO)$_4^-$

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The species Ni(CO)$_3^-$, Cr(CO)$_5^-$, and Fe(CO)$_4^-$ are prepared in inert-gas matrices at 10 K by three methods: (i) vacuum-UV irradiation, (ii) bombardment with electrons, and (iii) cocondensation with alkali-metal atoms and subsequent photolysis. There is also evidence with the use of methods i and ii of carbonyl cations in the matrix. Analysis of the IR spectra obtained with the use of $^{13}C^{16}O/^{12}C^{16}O$ mixtures leads to the determination of a trigonal-planar structure (D_{3h}) for Ni(CO)$_3^-$, a square-pyramidal structure (C_{4v}) for Cr(CO)$_5^-$, and a C_{3v} structure for Fe(CO)$_4^-$. On photolysis of these anions with visible or UV radiation, photoionization occurs rather than loss of CO alone.

Introduction

There has been considerable interest recently in the preparation and properties of charged transition-metal carbonyl species. This group includes both relatively stable 18-electron species and unstable non-18-electron species. Ellis and coworkers, particularly, have synthesised some remarkable species of the first category; for instance, they have prepared[1] M(CO)$_4^{4-}$ anions (M = Cr, Mo, W) by the Na/NH$_3$ reduction of TMEDA M(CO)$_4$ and characterized them by vibrational spectroscopy.[2]

For the second category, which is the concern of this paper, several techniques have been used. Electrochemical[3,4] studies have provided strong evidence for the transient existence in solution of, among others, Cr(CO)$_5^-$, Mo(CO)$_5^-$, W(CO)$_5^-$, Cr(CO)$_6^+$, and Fe(CO)$_5^+$; although no vibrational spectra were obtained, ESR confirmed the presence of Cr(CO)$_6^+$ (g = 1.945). Among other ESR studies, we might mention that a broad signal (g = 1.945), obtained on mixing phenyllithium and (OC)$_5$Cr(OMe)Ph in an ESR cavity, is assigned[5] to Cr(CO)$_5^-$. Some unpublished data[6a] show that reduction of Fe(CO)$_5$ by Na/Hg gives several anion radicals including Fe$_2$(CO)$_8^-$ but no evidence for Fe(CO)$_4^-$, although there is other unpublished[6b] work which shows ESR evidence for a carbonyl anion, perhaps Fe(CO)$_4^-$, on electron addition via ionizing radiation to dilute solid Fe(CO)$_5$ in butyl THF. Ion cyclotron resonance[7,8] has provided considerable data on photochemical properties in an ideal unperturbed gas-phase environment. Mass spectrometry[9] and laser photoelectron spectrometry[10] give energetic information.

However, none of these methods has given positive structural information although some interesting structural conclusions can sometimes be drawn. For example, by analogy with the isostructural Co(CO)$_4$,[11] the g values for Fe(CO)$_4^-$ suggest a C_{3v} structure with the lone electron in the d$_{z^2}$ orbital;[6] ICR combined with photolysis with polarized light[7] indicates that Fe(CO)$_4^-$ has a nontetrahedral geometry.

The ideal structural method—X-ray crystallography—is irrelevant for unstable species, and, moreover, structural perturbation by the counterion can be very important.[12] The same problem of counterion perturbation is also very significant in vibrational spectroscopic studies on stable species in both solid and solution,[13,14] and, even in the absence of counter ion perturbation, the vibrational spectrum is sensitive to solvent.[15]

It has been shown previously[16] how valuable is the low-temperature matrix-isolation technique combined with vibrational spectroscopy, particularly using ^{13}CO isotopic enrichment, for examining the preparation, structure, and photochemistry of many simple metal carbonyls and unstable coordinatively unsaturated fragments. The solid noble-gas environment in these studies provides minimal spectral and structural perturbation and hence would be ideal for examining the properties of unstable carbonyl ions. In fact, we have given preliminary reports of such investigations.[17,18]

Several matrix-isolation studies have demonstrated the value of the matrix technique to a wide variety of ionic species;[19] of possible routes to generating ions in a matrix environment, three are of particular relevance to the work reported here.

(a) Kasai[20] condensed sodium atoms with B$_2$H$_6$/Ar mixtures at 20 K and after photolysis with $\lambda > 500$ nm observed the ESR spectrum of B$_2$H$_6^-$. We have reported[17] a similar approach using Cr(CO)$_6$/Ar mixtures which leads to production of the new species Cr(CO)$_5^-$.

(b) Jacox and Milligan have used vacuum-UV irradiation

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of matrix-isolated samples to produce, e.g., NO_2^- from NO_2/Ar mixtures[21] and C_2^- from C_2H_2 trapped in argon.[22] We have previously communicated our results[18] concerning the matrix synthesis of $Ni(CO)_3^-$ from $Ni(CO)_4$ using this route.

(c) Electron bombardment has also been used to produce ions from neutral molecules. For example, Andrews[19] cocondensed CCl_4/Ar mixtures with a high-energy beam of electrons and observed the CCl_3^- ion.

All processes are basically ways of introducing electrons into the matrix: via photoionization of a low ionization potential metal (a), photoionization of stable molecules (b), or provision of the energy necessary to ionize the molecule as the kinetic energy of a light particle (c). Process c may result to some extent in electrons directly introduced into the matrix.

In this paper we shall build on our preliminary reports in this field and present detailed evidence for the new unstable species $Ni(CO)_3^-$, $Cr(CO)_5^-$, and $Fe(CO)_4^-$ produced by methods a–c above. As a test of the method we also present evidence for the matrix generation of the well-known anion $V(CO)_6^-$. All experimental details concerning our experiments appear in a section at the end of the paper.

Results and Discussion

$V(CO)_6^-$. One of the difficulties associated with matrix-isolation studies of charged species is being able to point to one set of bands due to an AB_n unit and conclude that this is a neutral molecule but another set of bands also describing an AB_n unit (perhaps of different geometry) are due to a charged AB_n^+ ion, for example. One initial experiment we consider then is the matrix synthesis of the $V(CO)_6^-$ ion from $V(CO)_6$ using one of the techniques outlined above. This ion is a well-known stable species, known at room temperature under a variety of conditions. It exhibits[15] a single carbonyl region stretching band at 1860 cm^{-1} (acetone solution) or 1843 cm^{-1} (THF solution), consistent with its regular octahedral symmetry. $V(CO)_6$ itself gives rise to an absorption in an Ar matrix at 1976 cm^{-1} (actually split by matrix effects), and this shift to lower frequency on anion formation is a feature of carbonyl anions in general. Carbonyl cations by way of contrast give IR bands to higher frequency than neutral carbonyls. The frequency of anion and cation carbonyl bands then is a vital clue as to the charge on the carbonyl species itself. A discussion of the magnitude of neutral/ion carbonyl band shifts is taken up later as further confirmation of the assignment of spectra.

Gas-phase mixtures of $V(CO)_6$ and Ar are very unstable and deposit vanadium metal very quickly. The only method of matrix isolation open to us is the pulsed-deposition route which excludes attempts at ion production using the cocondensation methods employing sodium or high-energy electrons. However, on 20-min vacuum-UV irradiation of a pulse-deposited sample ($V(CO)_6$:Ar = 1:3000), the spectral changes observed in the carbonyl stretching region are shown in Figure 1. All the new bands between 1890 and 2000 cm^{-1} appear on UV photolysis[23] of matrix-isolated $V(CO)_6$ and on cocondensation of V atoms with CO/Ar mixtures.[24] They have been assigned to $V(CO)_5$ and $V(CO)_4$ fragments derived by loss of CO from the parent molecule. However, the band observed at 1864 cm^{-1} is a feature induced by vacuum-UV radiation alone and is very close to the band observed for $V(CO)_6^-$ in acetone solution.[15]

Without doubt the new matrix species is also $V(CO)_6^-$. A band about 1/50th the intensity of this absorption is seen at 2070 cm^{-1} after the vacuum-UV irradiation. This is perhaps due to $V(CO)_6^+$ (probably octahedral with one IR-active CO stretch) or some other carbonyl cation necessary to preserve the electrical neutrality of the matrix. In general as the vibrational frequency of a CO stretching band decreases, its extinction coefficient increases so that the difference in intensity of these two bands could easily mean that their concentrations are similar. In experiments with vacuum-UV radiation and NO_2^- production, no spectral evidence was found[21] for the production of counterions (e.g., NO_2^+). Thus, in addition to the deliberately matrix-introduced molecule being able to provide electrons (e.g., $V(CO)_6$ in our present study), various low-concentration impurities are also photoelectron labile (as has to be the case in the NO_2^- experiment).

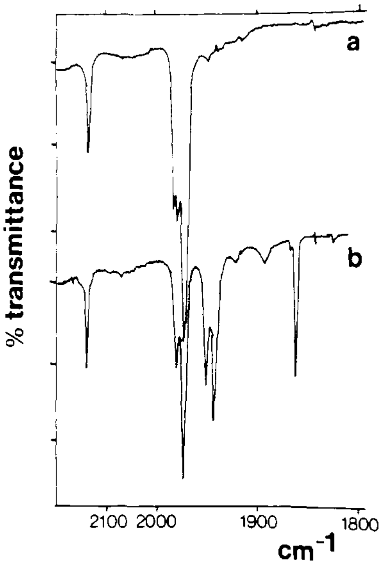

Figure 1. (a) $V(CO)_6$ trapped in an Ar matrix at 20 K. (b) Part a after 20-min of vacuum UV irradiation. (The band at ~2140 cm^{-1} is due to CO as a product of the gas-phase decomposition of the $V(CO)_6/Ar$ sample.)

On visible photolysis of matrix-isolated $V(CO)_6^-$, the 1864-cm^{-1} band disappears and $V(CO)_6$ is regenerated. There is no evidence for production of $V(CO)_5^-$ or other lower carbonyl anions. The photoelectron detachment process seems to be the preferred route in the matrix. Ion cyclotron resonance studies[8] however, show the existence of $V(CO)_5^-$, and Braterman[25] has evidence for the photoproduction of $V(CO)_5^-MeTHF$ from $V(CO)_6^-$ in MeTHF glasses at 77 K. Capture of another electron by $V(CO)_6^-$ itself is an unlikely event on two counts. First, the new species would contain 19 electrons and be unstable, and, second, the electrons percolating through the matrix will avoid sites of negative charge. One interesting point concerning the structure of $V(CO)_6$ and $V(CO)_6^-$ is that the band width of the anion band is significantly narrower than that of $V(CO)_6$ itself. Recall that the latter is predicted to have a low-energy (dynamic) Jahn–Teller distortion[26] and, although probably frozen out at 10 K, results in a small enough static distortion to split the degeneracy of the t_{1u} vibration of the O_h point group.

$Ni(CO)_3^-$. In contrast to vanadium, no stable binary carbonyl ion of nickel is known. However, we have presented[18] evidence for the production of $Ni(CO)_3^-$ via vacuum-UV photolysis of matrix-isolated $Ni(CO)_4$. After 20-min photolysis, three new bands are produced at 2178, 2016, and 1858 cm^{-1}. (Further irradiation resulted in a decrease in intensity

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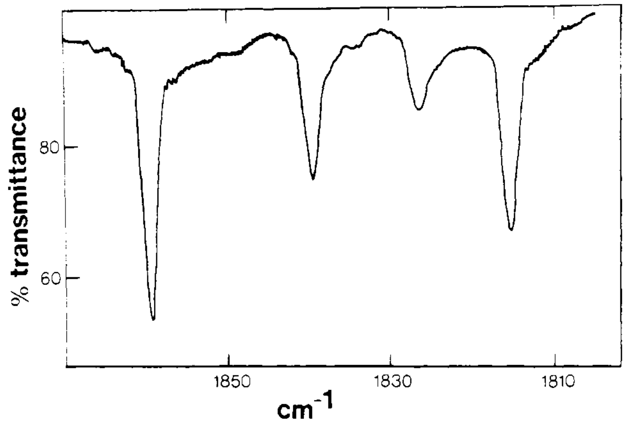

Figure 2. Isotopic spectrum of $Ni(^{12}CO)_x(^{13}CO)_{3-x}^-$ molecules.

Table I. Observed and Calculated Frequencies (cm^{-1}) for $Ni(CO)_3^-$ in Argon at 20 K

obsd	calcd^a I	calcd^b II
1857.9	1856.4	1857.5
1838.3	1839.2	1839.3
1825.6	1826.0	1825.6
1814.7	1815.0	1814.2
mean error, cm^{-1}	0.90	0.59
k_{CO}, N m^{-1}	1459.62	1461.44
k_{COCO}, N m^{-1}	67.42	67.65
$[\mu(^{13}CO)/\mu(^{12}CO)]^{1/2}$	0.977 709	0.976 693

^{a} Here the reduced mass ratio is not allowed to vary. The poor fit is mainly due to the fact that the frequency of the totally ^{13}CO-substituted molecule is not given exactly by using the frequency factored force field and the frequency of the ^{12}CO parent. ^{b} The reduced mass ratio is allowed to vary. The frequency fit is much improved and the force constants little different from I.

of two of these.) The two lower frequency bands may also be produced on cocondensation of Na atoms with an Ar/$Ni(CO)_4$ mixture at 20 K. The 2016-cm^{-1} band is due to $Ni(CO)_3$ and may readily be produced either by UV photolysis of matrix-isolated $Ni(CO)_4$[27] or condensation of Ni atoms with Ar/CO mixtures at 20 K.[28] The position of the low-frequency band (~160 cm^{-1} to lower frequency of $Ni(CO)_3$) indicates that a negative ion has been formed (see Discussion). The position of the high-frequency band, almost exactly where CO^+ is expected to absorb in the matrix,[29] led us previously to tentatively assign this band to this diatomic cation. On isotopic substitution, however (starting from an $Ni(^{12}CO)_x(^{13}CO)_{4-x}$ mixture), this weak high-frequency band appears to split into more than two components, and thus its assignment to an $Ni(CO)_x^+$ cation is probably more likely. Because of the weakness of the spectra in the high-frequency region (for reasons outlined in the previous section), a detailed structural analysis of this species was unfortunately not possible. On the other hand, the isotopic pattern associated with the 1858-cm^{-1} band is unequivocally interpreted (Figure 2) as being due to an $Ni(CO)_3$ unit containing a threefold axis (i.e., where all three groups are equivalent). It must belong to either C_{3v} or D_{3h} point groups. Use of the frequency factored force field and these observed isotopic frequencies allows us to predict the position of the high-frequency (a_1 or a_1') band associated with this $Ni(CO)_3^-$ molecule (Table I). A search of this particular region in the spectrum for this absorption was abortive, and we conclude therefore that the molecule is planar (D_{3h}) within experimental error. Interestingly, the isoelectronic molecule $Cu(CO)_3$ has recently been synthesized[30] in a matrix by Ozin and co-workers by cocondensing Cu atoms with a CO/Ar mixture. The planar D_{3h} geometry of the ion is in accord with modern ideas[31] and molecular orbital calculations concerning the geometries of transition-metal complexes.

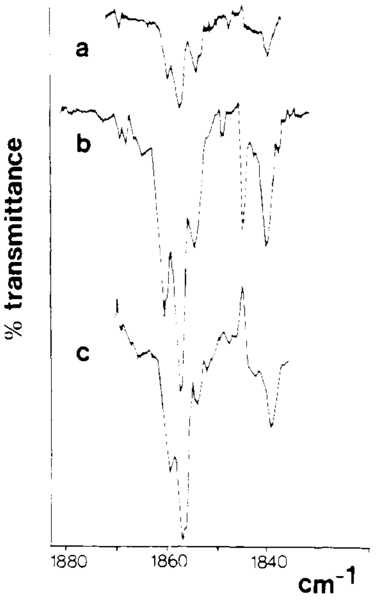

Figure 3. Infrared spectra of $Cr(CO)_5^-$ in an argon matrix produced by (a) cocondensation with sodium atoms and visible photolysis, (b) electron bombardment, and (c) vacuum-UV irradiation of $Cr(CO)_6$ in argon.

$M(CO)_5^-$ (M = Cr, Mo, W). We have previously reported[17] our preliminary finding on the spectrum of $Cr(CO)_5^-$. In this section we present evidence that this species adopts a square-pyramidal structure.

Figure 3a shows the IR spectrum in the region 1800–1880 cm^{-1} after sodium atoms have been cocondensed with a $Cr(CO)_6$/Ar mixture (1:3000) with simultaneous UV–visible photolysis from a medium-pressure mercury lamp. (Photolysis after deposition is not very efficient due to absorption of the radiation by the sodium atoms in the first few layers of the matrix.) Other infrared bands, which are not shown, are immediately identified as arising from $Cr(CO)_5$ and $Cr(CO)_4$.[32] When the experiment is repeated using potassium atoms, the spectra are almost identical. Using $Mo(CO)_6$ and $W(CO)_6$ gives very similar spectra in the same spectral region but with frequencies which are dependent upon the nature of the metal atom used. Thus we have definitely produced a new metal carbonyl containing anionic species. These experiments were repeated with alkali-metal atoms and CO-containing matrices to exclude the possibility of the bands being associated with Na/CO species. Only with reasonably high concentrations of alkali-metal atoms were any new spectral features observed: a broad intense absorption centered at approximately 1900 cm^{-1} and about 200 cm^{-1} wide. None of the much sharper features previously observed are therefore associated with alkali-metal/CO species.

On electron bombardment with simultaneous deposition of the $Cr(CO)_6$/Ar (1:3000) mixture, bands due to $Cr(CO)_5$,

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$Cr(CO)_4$, and $Cr(CO)_3$ are observed[32] in addition to the features at 1855 and 1838 cm^{-1} observed before (Figure 3b). Thus we may immediately conclude that the effect of the alkali-metal atoms on the band positions of the ion is small. In contrast to the metal experiments, some weaker bands are observed to high frequency at 2095 (s) and 2078 cm^{-1} (w). These bands may be assigned to carbonyl cations as before, whose role in the sodium atom experiments is played by the Na^+ ions themselves. So that polymeric materials could be excluded from consideration, the experiment was repeated with a $Cr(CO)_6/Ar$ mixture of 1:25 000 dilution. The spectra in all parts of the carbonyl region were identical with those obtained at the lower dilution. Vacuum-UV photolysis of deposited samples gives similar spectra (Figure 3c) and weak high-frequency bands associated with counterion production. In these experiments the amount of neutral carbonyl fragments produced was smaller than in the experiments with sodium atoms or electron bombardment.

The band pattern for the new anionic species consists of a strong doublet at 1857 and 1854 cm^{-1} (with a weak shoulder at 1860 cm^{-1}) and a single weaker band at 1839 cm^{-1}. The intensities of the two components at the higher frequency absorption depend upon the mode of preparation and history of the sample. Exposure of the sample produced by sodium atom cocondensation with $Cr(CO)_6/Ar$ to the medium-pressure Hg lamp leads to a situation where the 1857-cm^{-1} band is reduced in intensity and the 1854-cm^{-1} absorption is the stronger of the two. Annealing the matrix reimposes the initial intensity ratio. In the simultaneous photolysis spray-on experiments, the two components appear to be of the same intensity. In the electron bombardment experiments, the spectra are very similar to the sodium atom spectrum after annealing. This band pattern was stable to annealing. The spectra obtained after vacuum-UV irradiation are identical with those obtained by electron bombardment. After visible photolysis ($\lambda > 357$ nm), however, the lower frequency component of the higher frequency doublet is dramatically reduced in intensity. On photolysis with $\lambda > 310$ nm of samples produced either by electron bombardment or by vacuum-UV, all these features due to charged species disappeared and no new bands took their place. Thus there is no evidence for production of $Cr(CO)_4^-$ or any other lower carbonyl anions on photolysis in the matrix. (This is in contrast to ICR studies[7,8] where photolysis of $Cr(CO)_5^-$ leads to production of $Cr(CO)_4^-$.) (In the sodium atom experiments, the new bands did not disappear since photolysis of the sodium atoms present is a source of electrons in the matrix. A steady-state concentration of anions is formed by the vacuum-UV experiment since the discharge lamp also generates visible and UV radiation.) In general, however, the ratio of the sum of the intensities of the two higher frequency components to the intensity of the lower frequency band remains approximately constant. This indicates that these new spectral features are due to a single new species but are split by "matrix splittings" dependent upon the subtleties of the local matrix environment. Basically similar results, with slightly different splitting patterns, occur in other matrices, e.g., N_2 and CH_4. We comment further on these splittings a little later.

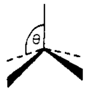
The two spectral features of the new anion are reminiscent of the low-frequency region of $Cr(CO)_5$ itself, and our analysis in the next section shows that the isotopic spectrum fits this square-pyramidal model very well. The 18-electron rule suggests that $Cr(CO)_6^-$ is an unlikely candidate, and the isotopic spectrum rules out species with less than four CO ligands since too many bands are observed.

Table II. Force Constants Obtained for $Cr(CO)_5^-$ ($N\ m^{-1}$)

	a	*b*		*a*	*b*
k_{ax}	1399	1391	cis k_{eq-eq}	39	26
k_{eq}	1445	1432	trans k_{eq-eq}	52	39
k_{eq-ax}	41	31			

[a] Values from the best fit obtained with an estimate of position of the high-frequency a_1 absorption. [b] Values from the best fit obtained with an estimate of the IR-inactive b_2 absorption.

Analysis of the Isotopic Spectrum. The ground rules for the interpretation and simulation of the isotopic spectrum of the new molecule (made by vacuum-UV photolysis of isotopically enriched $Cr(^{12}CO)_x(^{13}CO)_{6-x}$ in statistical abundance) are well-known in this field.[16,32-35] First, the band positions need to be fitted to a set of force constants with the use of the frequency factored force field, and, second, the relative intensities of all bands in the isotopic spectrum are calculated with use of this force field, the associated eigenvectors, and the local oscillating dipole method. One difficulty with the present situation is the breadth of the infrared bands and the presence of small splittings which produce difficulties in resolving and assigning all the bands of the isotopic spectrum. Another restriction on the method here is that no high-frequency bands are observed, without at least one of which the vibrational problem is underdetermined. The expected positions for these (weaker) bands is obscured by the much more intense low-frequency fundamentals of $Cr(CO)_5$ and $Cr(CO)_6$ themselves. We have tackled this problem in two ways. First, the position of the high-frequency a_1 vibration of a supposed square-pyramidal $Cr(CO)_5^-$ molecule was estimated at 1988 cm^{-1} by taking a weighted value from the observed figure for $Cr(CO)_5$ itself and the frequency difference between the e modes of $Cr(CO)_5$ and $Cr(CO)_5^-$. Second, the position of the IR-inactive b_2 vibration of the C_{4v} molecule $Cr(^{12}CO)_5^-$ was estimated to render the problem soluble. It was observed that in $Cr(CO)_5$ an IR absorption for the equatorially substitued $Cr(^{12}CO)_4(^{13}CO)$ molecule appears[32] 10 cm^{-1} below the calculated position of the inactive b_2 mode of the unsubstituted molecule. This band was the highest frequency absorption in low-frequency region and so was easily identified. In the present case, the highest frequency band of the isotopic spectrum in this region was observed at 1870 cm^{-1}. From this a frequency of 1880 cm^{-1} was estimated for the b_2 mode of the unsubstituted molecule. Both of these estimates led to a set of force constants from which an isotopic spectrum could be calculated and a least-squares refinement performed in the normal way. The two sets of force constants differ slightly, mainly in the values of the interaction constants (Table II). The main difference between the two solutions is the predicted position of the high-frequency vibrations which are, of course unobserved. The nonobservation of bands in this region means that the bond angle may not be calculated directly from the relative IR intensities as we have done previously for $Cr(CO)_5$ itself. However, use of $\theta = 95°$ (**1**) gives rise to a calculated spectrum (Figure 4) which is in good agreement as far as intensities are concerned with the observed pattern. A tabulation of the observed and calculated frequencies obtained with use of the two methods is given in Table III. The spectrum of the isotopic molecules is very different for a trigonal-bi-



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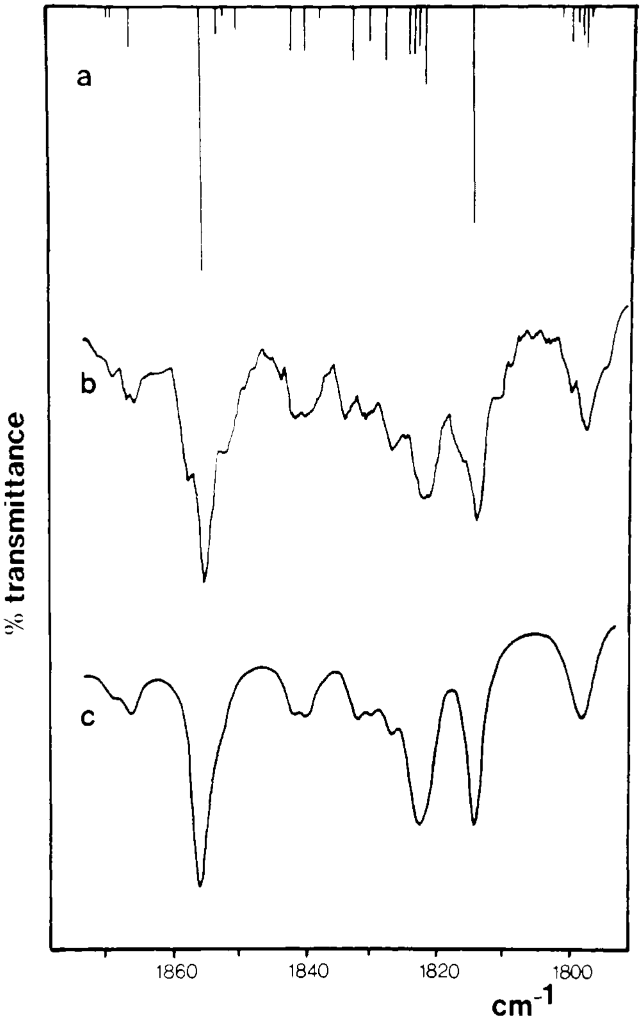

Figure 4. (a) Calculated "stick" spectrum (in relative optical density), (b) observed transmission spectrum, and (c) computer-simulated spectrum (Lorentzians with 3-cm^{-1} half-width) of isotopic C_{4v} Cr(CO)$_5^-$ molecules with a ^{12}CO:^{13}CO ratio of about 1.2. Axial–equatorial angle = 95°.

pyramidal geometry as we have shown previously, and this structure may definitely be eliminated from consideration. The observed isotopic spectrum could accommodate a small distortion to a C_{2v} structure which we would be unable to detect because of the breadth of the bands, but basically the spectrum is consistent with a C_{4v} square-pyramidal Cr(CO)$_5^-$ unit. This is the structure predicted[31] for a low-spin d^7 carbonyl and previously observed for the isoelectronic Mn(CO)$_5$ molecule.[36] The tbp geometry is expected and observed for the d^8 molecules, e.g., Fe(CO)$_5$, Mn(CO)$_5^-$, Cr(CO)$_5^{2-}$.

We can come to no conclusion about the cation identity since the bands are very weak. Only one band is observed with small matrix splittings when Cr(^{12}CO)$_6$ is used which may be indicative of an octahedral Cr(CO)$_6^+$ species.

Fe(CO)$_4^-$. When a gas-phase Fe(CO)$_5$/Ar (1:2000) mixture is cocondensed with sodium atoms onto a cold window at 20 K and simultaneously photolysed with a medium-pressure mercury lamp, new bands betweeen 2050 and 1950 cm^{-1} appear characteristic of the Fe(CO)$_4$ molecule.[37] In addition two strong new bands, not assignable to a neutral binary carbonyl, appear at 1864.2 and 1854.1 cm^{-1} (with a shoulder to low frequency) (Figure 5). These new bands lie between those of Fe(CO)$_4$ and Fe(CO)$_4^{2-}$ and are therefore assigned to an Fe(CO)$_x^-$ ion with a single charge (Table VI and Discussion). With use of the electron bombardment method, bands due to Fe(CO)$_4$, Fe(CO)$_3$, and Fe(CO)$_2$[38] were also produced in addition to these two strong absorptions. To high frequency were observed three new bands, 2116, 2124, and 2127 cm^{-1}, in the region associated with carbonyl cations. On UV–vis photolysis, these cation and anion bands rapidly disappeared and no new absorptions occurred in their place.

Table III. Calculated[d] and Observed Frequencies for Cr(CO)$_5^-$

molecule (sym)	sym of vib	frequency, cm^{-1}	
		calcd	obsd
Cr(^{12}CO)$_5$ (C_{4v})	a$_1$	1839.4	1839.1
	a$_1$	1957.5	*a*
	b$_2$	1875.0	IR inactive
	e	1857.5	1857.1
Cr(^{12}CO)$_4$(^{13}CO) (C_{4v})	a$_1$	1802.6	1800.4
	a$_1$	1953.0	*a*
	b$_2$	1875.0	IR inactive
	e	1857.5	1857.1
Cr(^{12}CO)$_4$(^{13}CO) (C_s)	a′	1841.5	1842.0
	a′	1824.5	1823.9
	a′	1950.7	*a*
	a′	1870.8	1871.0
	a″	1857.5	1857.1
Cr(^{12}CO)$_3$(^{13}CO)$_2$ (C_s)	a′	1800.8	*b*
	a′	1828.8	1828.5
	a′	1945.7	*a*
	a′	1870.7	*b*
	a″	1857.5	1857.1
Cr(^{12}CO)$_3$(^{13}CO)$_2$ (C_s)	a′	1843.7	1843.6
	a′	1825.7	*b*
	a′	1942.7	*a*
	a″	1868.0	1867.7
	a″	1822.9	1822.7
Cr(^{12}CO)$_3$(^{13}CO)$_2$ (C_{2v})	a$_1$	1854.2	*b*
	a$_1$	1831.7	*b*
	a$_1$	1943.4	*a*
	b$_2$	1816.1	1815.6
	b$_1$	1857.5	1857.1
Cr(^{13}CO)$_3$(^{12}CO)$_2$ (C_{2v})	a$_1$	1800.0	*b*
	a$_1$	1938.0	*a*
	a$_1$	1850.0	*b*
	b$_1$	1857.5	1857.1
	b$_2$	1816.1	1815.6
Cr(^{13}CO)$_3$(^{12}CO)$_2$ (C_s)	a′	1799.6	1799.4
	a′	1937.2	*a*
	a′	1834	1835.7
	a″	1822.9	1822.7
	a″	1868.0	1867.7
Cr(^{13}CO)$_3$(^{12}CO)$_2$ (C_s)	a′	1855.2	*b*
	a′	1933.9	*a*
	a′	1831.8	1832.4
	a′	1824.0	*b*
	a″	1816.1	1815.6
Cr(^{13}CO)$_4$(^{12}CO) (C_s)	a′	1799.0	1798.6
	a′	1927.5	*a*
	a′	1852.1	*b*
	a′	1825.0	*b*
	a″	1816.1	1815.6
Cr(^{13}CO)$_4$(^{12}CO) (C_{4v})	a$_1$	1922.3	*a*
	a$_1$	1831.4	*b*
	b$_2$	1833.2	IR inactive
	e	1816.1	1815.6
Cr(^{13}CO)$_5$ (C_{4v})	a$_1$	1798.4	1798.0[c]
	a$_1$	1913.9	*a*
	b$_2$	1833.2	IR inactive
	e	1816.1	1815.6

[a] Unobserved. [b] Unresolved. [c] Observed in 80% ^{13}CO enrichment experiment. [d] Using initial estimate of position of the b$_2$ of the unsubstituted molecule.

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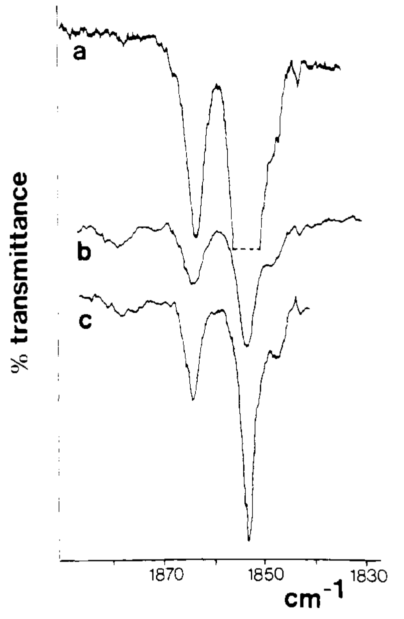
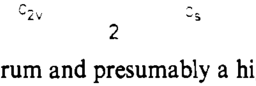


Figure 5. Infrared spectrum of $Fe(CO)_4^-$ in an argon matrix produced by (a) cocondensation with sodium atoms and visible photolysis, (b) electron bombardment, and (c) vacuum-UV irradiation.

Again this differs from ICR[7] which indicates CO loss on photolysis of $Fe(CO)_x^-$.

These experiments were repeated with a dilution of 1:25 000 and identical results obtained, thus eliminating the possibility of dimer and polymer formation. Very similar spectra were obtained with the use of vacuum-UV photolysis of the matrix-isolated sample. As usual, we need to use isotopic substitution to definitely identify the new species and elucidate its structure. Two possibilities are open to us, $Fe(CO)_4^-$ and $Fe(CO)_3^-$. Arguing by analogy with the Cr system, we find $Fe(CO)_4^-$ to be the more likely candidate.

Analysis of the Isotopic Spectrum. First, the isotopic spectrum is inconsistent with the presence of a pentacoordinate carbonyl species. The error between observed and calculated frequencies for the D_{3h} model was 2 cm^{-1} which is very high and immediately rules out this structure on frequency fit grounds alone. On this model also the calculated band intensities did not fit even qualitatively with the experimental ones. For the C_{4v} structure, there were too many bands in the spectrum for this to be likely. For a tricarbonyl species there are two possible structures (**2**) compatible with the pair of bands in the spectrum and presumably a high-frequency band obscured by the bands due to neutral $Fe(CO)_x$ fragments. A C_{3v} or D_{3h} structure (cf. $Ni(CO)_3^-$) would give rise to only one absorption (e) in this region. The best frequency fit obtainable by using the structures **2** was 1.2 cm^{-1} which suggests that neither of these structures is the correct one. In addition the calculated isotopic intensity pattern does not match the observed one at all well. This leaves a tetracarbonyl species. The isoelectronic molecule $Co(CO)_4$ has a C_{3v} structure[39] under most matrix conditions although a D_{2d} structure has been identified by ESR in a matrix.[40] Molecular orbital calculations[31] place these two structures very close together in energy for this electronic configuration with the D_{2d} slightly the more stable of the two. Both structures would give rise to low-frequency infrared absorptions in the CO stretching region (D_{2d}, $a_1 + b_2 + e$; C_{3v}, $2a_1 + e$), and the C_{3v} structure would also produce a band at higher frequency which would probably be obscured by the presence of absorptions due to neutral $Fe(CO)_x$ species present. The two structures with their necessary frequency factored force constants are shown in **3**.



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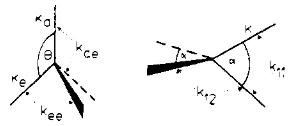

3

Since for the D_{2d} structure there are only two observed frequencies ($b_2 + e$) and three force constants, we need to make an initial approximation. The high-frequency (unobserved) band was estimated to be at around 1940 cm^{-1} by comparison with $Co(CO)_4$. The 1869.2-cm^{-1} band is then assigned to the b_2 and the 1859.1-cm^{-1} band to the e mode of the D_{2d} molecule. From the ratio of the intensities of these two bands and use of the relationship

$$\tan^2(\alpha/2) = I(e)/I(b_2)$$

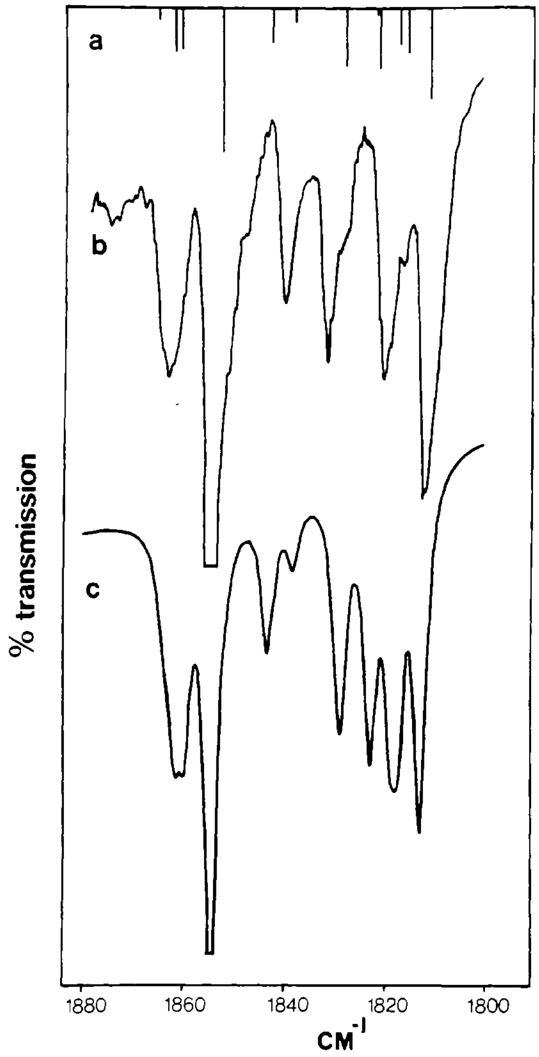

Figure 6. (a) Calculated "stick" spectrum (in relative optical density), (b) observed transmission spectrum, and (c) computer-simulated spectrum (Lorentzians with 3-cm^{-1} half-width) of isotopic D_{2d} $Fe(CO)_4^-$ molecules. The angle α (**3**) is 132°, and the frequency fit shown is the best obtained for this model. As may be seen, neither the frequencies nor relative intensities of the bands fits this model at all well. Compare this with Figure 7.

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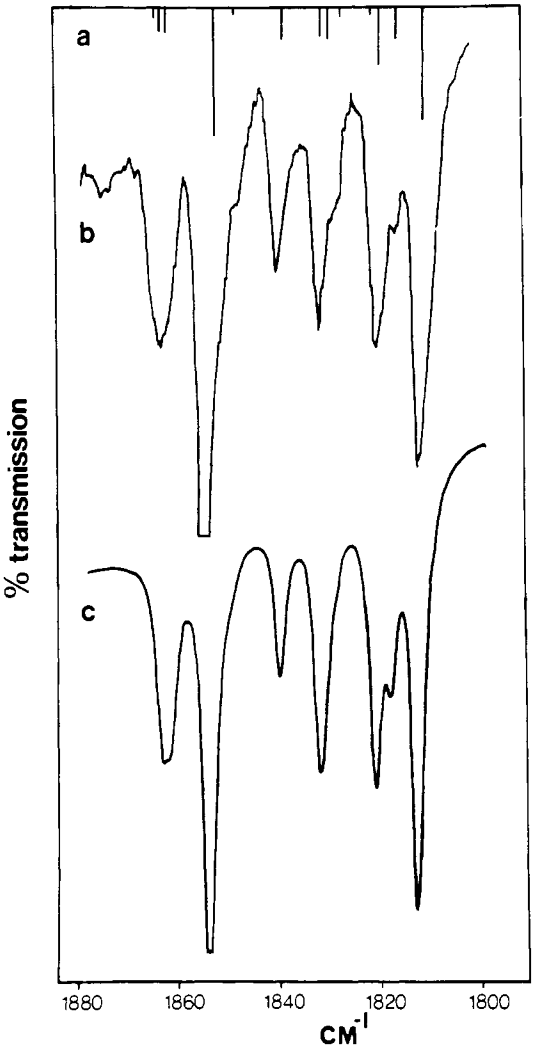

Figure 7. (a) Calculated "stick" spectrum (in relative optical density), (b) observed transmission spectrum, and (c) computer-simulated spectrum (Lorentzians with 3-cm^{-1} half-width) of isotopic C_{3v} Fe(CO)$_4^-$ molecules with a ^{12}CO:^{13}CO ratio of about 1.5. Axial–equatorial angle = 103°. Compare this figure with Figure 6.

α is calculated to be 132° (3). Refinement of the observed isotopic frequencies on this model gave an error of 1.7 cm^{-1} overall which is a poor fit, and in addition it gave rather bad agreement between the observed and calculated relative intensities of the isotopic spectrum when this force field and calculated band angle are used. Neither the frequency fit nor intensities of the bands is expected to be sensitive to our "guess" of the high-frequency a$_1$ band, and so one may rule out this structure altogether (Figure 6).

The C_{3v} structure is also underdetermined when we consider the parent Fe(^{12}CO)$_4^-$ molecule alone. We use here the estimated position of the high-frequency a$_1$ band and the cos β method developed by Bor[41] to estimate the values of the force constants of the parent molecule (cos β = 0.4 gave a reasonable fit). The observed vibrational frequencies were refined in the usual way, and a mean error of 0.62 cm^{-1} was obtained between observed and calculated frequencies. This good fit immediately gives us confidence in this structure, and indeed the features of the isotopic spectrum are well matched with θ of **3** equal to 103° (Figure 7). We cannot calculate the bond angle experimentally since for this we need the intensity of the missing high-frequency a$_1$ band. For Co(CO)$_4$, a C_{3v} structure was also found with $\theta \simeq$ 100°. (Molecular orbital calculations[31] locate the minimum in the C_{3v} energy coordinate at $\theta \simeq$ 100°, which is comforting.) A d^9 C_{3v} structure with $\theta > \theta_{\text{tet}}$ would be Jahn–Teller unstable. The calculated and observed frequencies are shown in Table IV and the force constants in Table V.

Table IV. Calculated and Observed IR Frequencies for for C_{3v} Fe(CO)$_4^-$

molecule (sym)	sym of vibratn	frequency, cm^{-1} calcd	obsd
Fe(^{12}CO)$_4$ (C_{3v})	a$_1$	1945.8	*a*
	a$_1$	1863.9	1864.2
	e	1853.7	1854.1
Fe(^{12}CO)$_3$(^{13}CO) (C_{3v})	a$_1$	1938.9	*a*
	a$_1$	1828.7	1828.8
	e	1853.7	1854.1
Fe(^{12}CO)$_3$(^{13}CO) (C_s)	a'	1937.6	*a*
	a'	1863.1	1863.3
	a'	1820.8	1819.8
	a''	1853.7	1854.1
Fe(^{12}CO)$_2$(^{13}CO)$_2$ (C_s)	a'	1929.6	*a*
	a'	1832.3	1831.7
	a'	1817.7	1816.3
	a''	1853.7	1854.1
Fe(^{13}CO)$_2$(^{12}CO)$_2$ (C_s)	a'	1928.3	*a*
	a'	1861.4	1862[b]
	a'	1831.2	1831.7
	a''	1812.4	1811.6
Fe(^{13}CO)$_3$(^{12}CO) (C_s)	a'	1918.2	*a*
	a'	1839.9	1840.5
	a'	1820.9	1821[b]
	a''	1812.4	1811.6
Fe(^{13}CO)$_3$(^{12}CO) (C_{3v})	a$_1$	1917.1	*a*
	a$_1$	1849.5	1850
	e	1812.4	1811.6
Fe(^{13}CO)$_4$ (C_{3v})	a$_1$	1902.4	*a*
	a$_1$	1822.3	*b*
	e	1812.4	1811.6

[a] Unobserved. [b] Incompletely resolved.

Table V. Force Constants (N m^{-1})[a] for C_{3v} Fe(CO)$_4^-$

k_a 1431	k_{ae} 30
k_e 1425	k_{ee} 38

[a] Force constants for best frequency fit on D_{2d} model: k = 1428, k_{11} = 41, k_{12} = 32 N m^{-1} (root-mean-square error 1.7 cm^{-1}).

Frequency Shifts for Neutral Ionic Carbonyl Species. It is important to establish whether the species identified as Ni(CO)$_3^-$, Cr(CO)$_5^-$, and Fe(CO)$_4^-$ display C–O stretching frequencies at positions which are reasonable compared with the usual neutral–ionic shifts. There are two obvious comparisons; one involves isoelectronic species, i.e., V(CO)$_6^-$, Cr(CO)$_6$, and Mn(CO)$_6^+$, and the other compares the effect of simply adding charge, e.g., Cr(CO)$_5$, Cr(CO)$_5^-$, and Cr(CO)$_5^{2-}$. In both cases, comparison is difficult because the frequencies are sensitive to environment, as mentioned in the Introduction. (For this reason it is difficult to apply Timney's[42] method with confidence, although work is in progress to refine his data.) Moreover, although for isoelectronic species it is reasonable to assume a similar structure, for the second comparative method the structure may well change.[31]

Table VI compares data for isoelectronic species; the solvent

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Table VI. IR Frequencies (cm^{-1}) of Some Carbonyl Species

$V(CO)_6^-$ (O_h) 1843^a (THF) 1845^a (CH_2Cl_2) 1860^a (acetone) 1864^d (Ar)	*130*	$Cr(CO)_6$ (O_h) 1984^a (CCl_4) 1987 (hydrocarbon) 1990^c (Ar)	*110*	$Mn(CO)_6^+$ (O_h) 2094^a (THF) 2102^b (HO_3SCF_3)		
$V(CO)_6$ 1976^d (Ar)	*119*	[$Cr(CO)_6^+$(?)] 2095^d (Ar)				
$Cr(CO)_5^{2-}$ (D_{3h}) 1760 (a_2'')^e (HMPA) 1722 (e')^e (HMPA)	*140*	$Mn(CO)_5^-$ (D_{3h}) 1898 (a_2'')^a (THF) 1863 (e')^a (THF)	*125*	$Fe(CO)_5$ (D_{3h}) 2022 (a_2'')^a (C_6H_{12}) 2000 (e')^a (C_6H_{12}) 2020 (a_2'')^a (CCl_4) 1995 (e')^a (CCl_4)		
$Cr(CO)_5^-$ (C_{4v}) 1855 (e)^d (Ar) 1838 (a_1)^d (Ar)	*135*	$Mn(CO)_5$ (C_{4v}) 1987 (e)^f (CO) 1978 (a_1) (CO)	*130*	[$Fe(CO)_5^+$(?)] 2120^d (Ar)		
$Cr(CO)_5$ (C_{4v}) 2093 (a_1)^c (Ar) 1965 (e) (Ar) 1933 (a_1) (Ar)	*130*	$Mn(CO)_5^+$ (C_{4v}) 2164 (a_1)^b (HO_3SCF_3) 2083 (e) (HO_3SCF_3) 2042 (a_1) (HO_3SCF_3)				
$Fe(CO)_4^{2-}$ (T_d) 1729^g (t_2) (HMPA) [1786^h (t_2) (H_2O)]	*160*	$Co(CO)_4^-$ (T_d) 1887^i (t_2) (THF)	*150*	$Ni(CO)_4$ (T_d) 2044^a (CCl_4) 2043^a (CO matrix) 2040^j (THF) 2052^d (Ar matrix)	*140*	$Cu(CO)_4^+$ (T_d) 2183^k (t_2) (FSO_3H)
$Fe(CO)_4^-$ (C_{3v}) 1864^d (Ar) 1854 (Ar)	*160*	$Co(CO)_4$ 2029^l (CO matrix) 2011 (CO matrix)	*150*	[$Ni(CO)_4^+$(?)] 2178^d (Ar)		
$Ni(CO)_3$ (D_{3h}) 2016^m (Ar)	*160*	$Cu(CO)_3^+$ (D_{3h}) 2177^k (FSO_3H)				
$Ni(CO)_3^-$ (D_{3h}) 1858^d (Ar)	*125*	$Cu(CO)_3$ (D_{3h}) 1985 (e')^n (Ar) 1976 (e') (Ar)				

[a] Frequencies taken from ref 15. [b] Reference 43. [c] Reference 32. [d] This work. [e] Reference 44. [f] Timney, J. A. Ph.D. Thesis, Newcastle, 1980, and ref 42. The quoted frequencies are different from those in: Huber, H; Ozin, G. A.; Kundig, E. P.; Poe, A J. *J. Am. Chem. Soc.* 1975, *97*, 308, which we believe to be in error. [g] Reference 45. [h] Reference 46. [i] This ion is easily perturbed by neighboring cations; the quoted value is for the anion completely surrounded by solvent.[13d] [j] Reference 47. [k] Reference 48. [l] This species exists in low-temperature matrices in both D_{2d} and C_{3v} forms; the quoted values are for C_{3v}.[39] [m] References 27 and 28. [n] Reference 30; $Cu(CO)_3$ occurs in two different matrix sites.

Table VII. Comparison of C–O Frequencies of Carbonyl Species

	$V(CO)_6$ $V(CO)_6^-$	$Cr(CO)_5$ $Cr(CO)_5^-$	$Mn(CO)_5$ $Mn(CO)_5^-$	$Fe(CO)_4$ $Fe(CO)_4^-$	$Co(CO)_4$ $Co(CO)_4^-$	$Ni(CO)_3$ $Ni(CO)_3^-$
Δ, cm^{-1}	112	110	124	111	124	158
	$V(CO)_6^+$ $V(CO)_6$	$Cr(CO)_6^+$ $Cr(CO)_6$	$Fe(CO)_5^+$ $Fe(CO)_5$	$Ni(CO)_4^+$ $Ni(CO)_4$	$Cu(CO)_3^+$ $Cu(CO)_3$	
Δ, cm^{-1}	94	105	98	114	197	

effect is striking for many species. Thus we should attempt to compare, where possible, data for the same environment. The italic numbers between the species represent an approximate value for the shift, bearing this point in mind. Without reading too much into the data, it is nonetheless clear that the assignments of bands to $Cr(CO)_5^-$ and $Fe(CO)_4^-$ is quite reasonable. Moreover, it is encouraging that the assignment of bands to $Fe(CO)_5^+$, $Cr(CO)_6^+$, and $Ni(CO)_4^+$ is consistent with the expected shifts. Only $Ni(CO)_3^-$ appears at a frequency that is perhaps surprising.

A comparison of data following the second method is given in Table VII from the data in Table VI and the text. Whether the symmetries are the same or different, we have simply compared the positions of the most intense bands. Again the $Ni(CO)_3^-$ seems somewhat out of line, but the shift from $Cu(CO)_3^+$ to $Cu(CO)_3$ is even greater, suggesting that where the "extra electron" does not enter the d shell, the simple correlation breaks down.

Mechanism of Ion Formation. There are two possible unimolecular processes which could lead to anion formation in the matrix by capture of an electron generated by photolysis of sodium atoms, high-energy bombardment, or vacuum-UV irradiation:

(a) Electron capture by a neutral molecule:

$$A + e^- \rightarrow A^-$$

(b) Dissociative electron capture by parent:

$$A\text{–}CO + e^- \rightarrow A^- + CO$$

In addition there is a third possibility open via vacuum-UV irradiation only:

(c) Heterolytic bond fission:

$$A\text{–}CO + \text{vacuum-UV} \rightarrow A^- + CO^+$$

Process c is probably the most unlikely. It was tentatively suggested[18] that $Ni(CO)_3^-$ and CO^+ were produced via the vacuum-UV photolysis of $Ni(CO)_4$ in Ar, and this was based on the appearance of a band in the high-frequency region with a frequency very similar to that predicted for CO^+. Isotopic substitution, however, did not lead to any firm conclusions as to the identify of the absorber due to the weakness of bands in this region. The energy required to break an M–CO bond

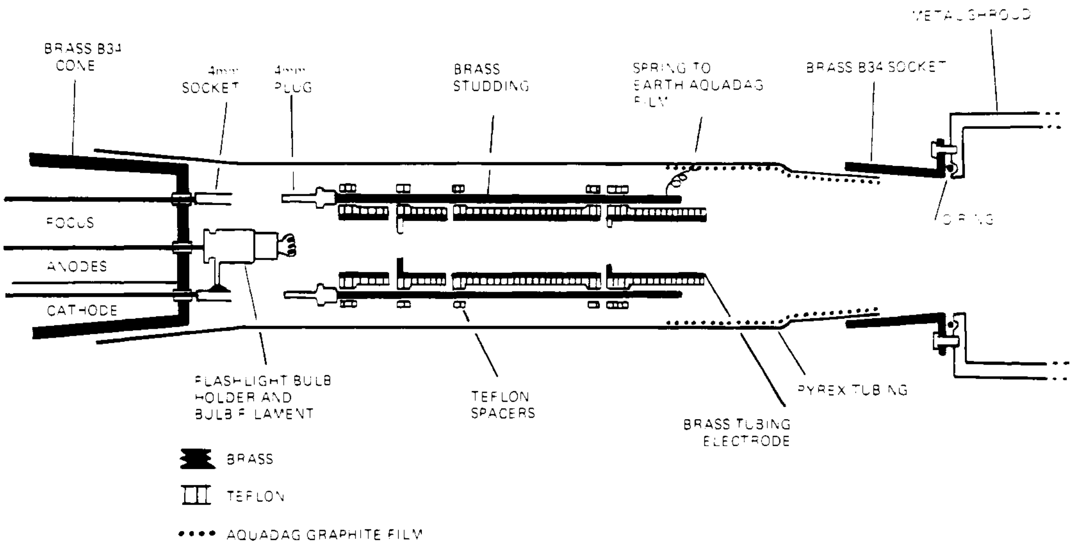

Figure 8. Electron gun assembley.

is about 1.5 eV, and the ionization potential of CO is 12 eV. If we assume that 1 eV is regained on attaching an electron to $Ni(CO)_3$, then in order to produce heterolytic fission one needs to provide 12.5 eV. The output of the H_2 lamp is only 10.2 eV, however. The difference would have to be made by the Coulombic attraction of the ions in the matrix. Numerically, this would be so if the ions were less than 6 Å apart, in which case it is difficult to understand why they do not immediately recombine. The alternative (and we believe more likely) explanation is that this band is due to a cationic carbonyl fragment. It fits into the general series of cation bands observed (Table VII) in these systems quite well. Process c cannot occur, of course, in experiments with sodium atoms and photolysis, but $Ni(CO)_3^-$ is made just as readily via this route.

Process b is open to all species where the parent molecule ion is unstable with respect to CO loss, and we expect this to be the case with the 19-electron species $Cr(CO)_6^-$, $Fe(CO)_5^-$, and $Ni(CO)_4^-$. Loss of a CO group to produce $Cr(CO)_5^-$, $Fe(CO)_4^-$, and $Ni(CO)_3^-$ would leave these systems with 17 electrons. Since all methods of anion production of $M(CO)_{x-1}^-$ from $M(CO)_x$ involve production of the neutral fragment $M(CO)_{x-1}$ in addition to charged species, we cannot rule out process a occurring as well as process b in these situations. Process a is of course the only one applicable to formation of 18-electron $V(CO)_6^-$ from 17-electron $V(CO)_6$ itself. Interestingly, no bands appear in the spectrum due to $V(CO)_5^-$ which implies that the $V(CO)_5$ itself, produced by the photolysis, has little chance of picking up an electron by process a.

Since three of the anions we have characterised are 17-electron species, they will be resistant to recombination with CO to give a higher anion. (Indeed they were probably produced by dissociative electron capture by the parent anyway.) The presence of this CO molecule in the same cage as the anion will perturb the infrared spectrum considerably, and we believe this is the reason for the splittings in the spectrum and its temperature behavior in the case of $Cr(CO)_5^-$ especially. With the neutral carbonyl fragments, these splittings may be removed by reversal of the $M(CO)_{x-1}$ fragment to the $M(CO)_x$ parent by visible photolysis and reirradiation with UV light. A sample of molecules where the CO is removed far enough away from the fragment on photolysis and does not recombine on visible photolysis or seriously perturb the infrared spectrum is accumulated. Perhaps this juxtaposition in the anion case means that on UV or visible photolysis loss of another CO molecule to give a 15-electron species is unlikely because rapid recombination to the 17-electron species may occur. Loss of the electron via photoionization is then the only observable process. In ion cyclotron resonance[7,8] experiments, photolysis of $M(CO)_{x-1}^-$ ions often lead to production of $M(CO)_{x-2}^-$.

Experimental Section

All experiments used an Air Products Displex CS202 refrigerator operating at about 10 K. The detailed setup is similar to that described previously.[32] Spectra were recorded with the use of Perkin-Elmer 521 and 125 spectrometers and were calibrated with DBr and DCl cells inserted in the beam before and after sample absorptions in the spectrum. Strong bands are reproducible to ±0.2 cm^{-1}, weak ones ±0.3 cm^{-1}. Matrix gases (BOC grade X) and metal hexacarbonyls (BDH) were used without further purification. $Fe(CO)_5$ (BDH), $Ni(CO)_4$ (BDH), and $V(CO)_6$ (Strem Chemicals) were subjected to a series of freeze–thaw cycles to remove CO before use. Isotopic enrichment followed standard methods[18,32,37] with 90% $^{13}C^{16}O$ (Prochem.). All calculations were performed on a Hewlett-Packard 2000E computer.

The alkali metal was evaporated from a small resistively heated cylindrical stainless-steel furnace containing a boat filled with metal (BDH). The end facing the cold window was closed off with the use of a stainless-steel nut through which a pinhole was drilled. At the other end was a facility for pumping on the chamber, necessary to outgas the metal, after filling and before experiments took place. The furnace temperature was monitored with use of a thermocouple—temperatures of 320–390 °C were found to be adequate for sodium and 270–300 °C for potassium. A rough calculation for a typical experiment gave an alkali metal:carbonyl:matrix ratio of about 50:1:3000. The matrix was slow sprayed on at about 3000 $cm^3\ h^{-1}$.

The electron gun used in the electron bombardment experiments is shown in Figure 8 which is almost self-explanatory. A flashlight bulb filament is used as a replaceable emitter, and the double anode, cathode, and focus sections allow the electron beam of adjustable energy to be defocused such that it covers the entire window. When no matrix was deposited, the unit could be tested with use of ZnS crystals glued to the radiation shield of the low-temperature system, but when condensed matrix was present, the blue, green, and yellow fluorescence of irradiated argon, nitrogen, or xenon, respectively, was sufficient to ensure correct operation. Accelerating voltages of 500–800 V were used during a slow sprayon experiment.

The vacuum-ultraviolet lamp consisted essentially of a hydrogen-discharge struck in a glass tube, arranged perpendicular to the cold window and sealed at that end with a LiF window (Specac) with the use of Torr-Seal (Varian). The tube had a pump out at the other end and a liquid-nitrogen cold finger to remove condensible impurities. The discharge was driven by a Microtron 200 microwave generator and gave radiation at 122 nm (10.2 eV).

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Registry No. $Ni(CO)_3^-$, 51222-94-7; $Cr(CO)_5^-$, 39586-86-2; $Fe(CO)_4^-$, 71564-27-7; $Cr(^{12}CO)_4(^{13}CO)^-(C_{4v})$, 78307-67-2; $Cr(^{12}CO)_4(^{13}CO)^-(C_s)$, 78341-41-0; $Cr(^{12}CO)_3(^{13}CO)_2^-(C_s)$, isomer 1, 78307-68-3; $Cr(^{12}CO)_3(^{13}CO)_2^-(C_s)$, isomer 2, 78341-42-1; $Cr(^{12}CO)_3(^{13}CO)_2^-(C_{2v})$, 78341-43-2; $Cr(^{13}CO)_3(^{13}CO)_2^-(C_{2v})$, 78307-69-4; $Cr(^{13}CO)_3(^{12}CO)_2^-(C_s)$, isomer 1, 78341-44-3; $Cr(^{13}CO)_3(^{12}CO)_2^-(C_s)$, isomer 2, 78341-45-4; $Cr(^{13}CO)_4(^{12}CO)^-(C_s)$, 78307-70-7; $Cr(^{13}CO)_4(^{12}CO)^-(C_{4v})$, 78341-46-5; $Cr(^{13}CO)_5^-(C_{4v})$, 78307-71-8; $Fe(^{12}CO)_3(^{13}CO)^-$, 78307-72-9; $Fe(^{12}CO)_2(^{13}CO)_2^-$, 78307-73-0; $Fe(^{13}CO)_3(^{12}CO)^-$, 78307-74-1; $Fe(^{13}CO)_4^-$, 78307-75-2; $V(CO)_6^-$, 20644-87-5; $V(CO)_6$, 14024-00-1; $Ni(CO)_4$, 13463-39-3; $Cr(CO)_6^+$, 54404-20-5; $Fe(CO)_5^+$, 59699-78-4; $Ni(CO)_4^+$, 71837-09-7.

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The First P^V–P^V Compound:[1] Bis(cyclenphosphorane), $(C_8H_{16}N_4P)_2$

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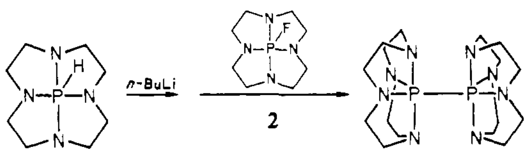
Synthetic routes leading to the formation of the first P^V–P^V compound, bis(cyclenphosphorane) $(C_8H_{16}N_4P)_2$ (**3**), are described. The coupling reaction between the lithiated derivative of cyclenphosphorane (**1**) and cyclenfluorophosphorane (**2**) yields **3**. Bis(cyclenphosphorane) has also been detected as one of the products formed in the reaction of **1** and benzyl bromide. Single-crystal X-ray diffraction analysis shows that the macrocyclic nitrogen-containing ligands, $N_4(CH_2)_8$, are arranged around the phosphorus atoms, giving a pentacoordinate geometry displaced 33% from the idealized trigonal bipyramid toward the square pyramid. **3** crystallizes in the orthorhombic space group *Ccca*, with $a = 14.777$ (6) Å, $b = 14.549$ (6) Å, $c = 8.664$ (3) Å, and $Z = 4$. Data were collected with an automated Enraf-Nonius CAD 4 diffractometer, out to a maximum $2\theta_{\mathrm{Mo}\,K\bar{\alpha}}$ of 55°. Full-matrix least-squares refinement techniques led to the final agreement factors of $R = 0.038$ and $R_w = 0.055$ based on the 850 reflections having $I \geq 2\sigma_I$. A P–P bond length of 2.264 (2) Å was obtained, indicating normal stability of the P^V–P^V bond. The two symmetry related halves of the molecule are rotated 70° relative to each other, presumably to minimize steric interactions. The P–P midpoint is on a crystallographic 222 site.

Introduction

The recent insertion of a phosphorus atom into macrocyclic polyamines[2] leading to tetraaminophosphoranes has provided a novel synthetic route to new classes of phosphorus compounds.[3] In a preliminary report,[4] we described a coupling reaction between the lithiated derivative of cyclenphosphorane (**1**) and cyclenfluorophosphorane (**2**) that resulted in the formation of the first P^V–P^V compound, bis(cyclenphosphorane) (**3**), $(C_8H_{16}N_4P)_2$. The proposed polycyclic structure of **3** was confirmed by X-ray analysis.[4]



1 **3**

In this paper we report details of this synthesis and an alternate route as well as the complete structural analysis of **3** resulting from a single-crystal X-ray diffraction study.

Experimental Section

Synthesis. Bis(cyclenphosphorane) (3) from 2 and the Lithiated Derivative of 1. The lithiation of cyclenphosphorane (**1**) was accomplished by adding an equivalent (0.9 mL) of 1.6 M *n*-butyllithium in hexane to a slurry of 275 mg (1.37 mmol) of cyclenphosphorane[3a] in 3 mL of anhydrous tetrahydrofuran stirred at −78 °C. The mixture was warmed to 20 °C, and 300 mg of crystalline cyclen fluorophosphorane[2] (**2**) was added followed by refluxing for 1 h. The mixture was concentrated under nitrogen and the residue sublimed in a bulb-to-bulb distillation apparatus, giving 150 mg (27% yield) of crystals of **3** collected at an oven temperature of 180–190 °C (0.1 mm): mp (sealed capillary) 320–330°; mass spectra M^+ 398 (5.2), 39 (1.1), 219 (3.6), 218 (5.3), 217 (1.5), 201 (1.8), 200 (23.6), 199 (100), 198 (6.1), 197 (5.0); ^1H NMR ($CDCl_3$), 2.5–3.3 ppm (br symmetrical m); ^{31}P NMR (C_6D_6) −36.8 ppm (upfield from 85% H_3PO_4); IR (KBr) 2830 (br, s), 1459 (w), 1360 (w), 1342, 1334, 1244, 1232, 1201 (s), 1192 (s), 1130 (s), 1070 (s), 880, 865, 751, 676, 593, and 473 cm^{-1} (w); UV (cyclohexane) sh 225 (ϵ 2370), end absorbance. Anal. Calcd for $C_{16}H_{32}N_8P_2$: C, 48.23; H, 8.10; N, 28.13 Found: C, 48.48; H, 8.55, N, 28.65.

Bis(cyclenphosphorane) (3) from the Reaction of Benzyl Bromide with the Lithiated Derivative of 1. A solution of 2.0 g of **1**[3a] in 30 mL of anhydrous tetrahydrofuran was lithiated as above (6.5 mL 1.6 M *n*-BuLi/−78 → 0 °C) and then was cooled to −78 °C and treated dropwise with 1.2 mL of benzyl bromide. This mixture was stirred overnight at 25 °C and then was refluxed for 2 h and concentrated. The residue was dissolved in hexane and filtered, and the solids were washed several times with hexane. The combined washes and filtrates were concentrated and distilled bulb-to-bulb. The first fraction collected at 80 °C (0.1 mm) (3 h) (0.79 g) was shown by NMR to be 1,2-diphenylethane contaminated with 10–15% of recovered **1**. A second fraction collected at 100–105 °C (0.1 mm) (1.0 g) was identified as the expected phosphorus benzylated product, cyclenbenzylphosphorane: mass spectrum *m/e* 290 (0.3%); ^1H NMR 5.28 (d, 16, $J_{PH} = 11$ Hz), 3.1 (d, 2, $J_{PH} = 18$ Hz), and 7.2 (s, 5); and ^{13}C NMR 44.2 (NCH_2, $J_{PC} = 8.8$ Hz), 42.3 (PCH_2, $J_{PC} = 138.3$ Hz), and aryl ring carbons (J_{PC}) at 124.9 (4.4 Hz), 127.3 (3.0 Hz), 130.3 (5.9 Hz) and (weak?) 138 ppm. A third fraction in the bulb-to-bulb distillation at 120–180 °C (0.1 mm) gave 10 mg of crystals shown by melting point and mass spectroscopy to be bis(cyclenphosphorane) (vide *supra*).

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