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Registry No. $Cr(CO)_5CS$, 50358-90-2; $W(CO)_5CS$, 50358-92-4; η^5-$C_5H_5Mn(CO)_2CS$, 31741-76-1.

References and Notes

(1) M. C. Baird and G. Wilkinson, *Chem. Commun.*, **9**, 267 (1966).
(2) M. C. Baird, G. Hartwell, and G. Wilkinson, *J. Chem. Soc. A*, 2037 (1967).
(3) M. P. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, 2813 (1968).
(4) J. D. Gilbert, M. C. Baird, and G. Wilkinson, *J. Chem. Soc. A*, 2198 (1968).
(5) L. Busetto and R. J. Angelici, *J. Am. Chem. Soc.*, **90**, 3283 (1968).
(6) L. Busetto, U. Belluco, and R. J. Angelici, *J. Organomet. Chem.*, **18**, 213 (1969).
(7) I. S. Butler and A. E. Fenster, *Chem. Commun.*, 933 (1970).
(8) A. E. Fenster and I. S. Butler, *Can. J. Chem.*, **50**, 598 (1972).
(9) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **95**, 7516 (1973).
(10) A. E. Fenster and I. S. Butler, *Inorg. Chem.*, **13**, 915 (1974).
(11) I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, **51**, 307 (1973).
(12) G. M. Bodner, *Inorg. Chem.*, **13**, 2563 (1974).
(13) N. Jonathan, A. Morris, M. Okuda, D. J. Smith, and K. J. Ross, *Chem. Phys. Lett.*, **13**, 334 (1972).
(14) G. H. King, H. W. Kroto, and R. J. Suffolk, *Chem. Phys. Lett.*, **13**, 457 (1972).
(15) D. C. Forst, S. T. Lee, and C. A. McDowell, *Chem. Phys. Lett.*, **17**, 153 (1972).
(16) W. G. Richards, *Trans. Faraday Soc.*, **63**, 257 (1967).
(17) M. Kubota and C. J. Curtis, *Inorg. Chem.*, **13**, 2277 (1974).
(18) I. S. Butler and D. A. Johansson, *Inorg. Chem.*, **14**, 701 (1975).
(19) D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, **8**, 2544 (1969).
(20) B. R. Higginson, D. R. Lloyd, P. Burroughs, D. M. Gibson, and A. F. Orchard, *J. Chem. Soc., Faraday Trans., 2*, **69**, 1659 (1973).
(21) B. R. Higginson, D. R. Lloyd, J. A. Connor, and I. H. Hillier, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1418 (1974).
(22) S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discuss. Faraday Soc.*, **47**, 112 (1969).
(23) D. L. Lichtenberger, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, **12**, 702 (1973).
(24) D. L. Lichtenberger and R. F. Fenske, *Inorg. Chem.*, **13**, 486 (1974).
(25) S. Cradock, E. A. V. Ebsworth, and A. Robertson, *J. Chem. Soc., Dalton Trans.*, **22** (1973).
(26) I. H. Hillier, M. F. Guest, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, **27**, 215 (1974).
(27) I. H. Hillier and V. R. Saunders, *Mol. Phys.*, **22**, 1025 (1971).
(28) M. F. Guest, M. B. Hall, and I. H. Hillier, *Mol. Phys.*, **25**, 629 (1973).
(29) D. L. Lichtenberger, Ph.D. Thesis, University of Wisconsin, 1974.
(30) (a) R. K. Nesbet, *J. Chem. Phys.*, **43**, 4403 (1965); (b) W. M. Huo, *ibid.*, **43**, 624 (1965).
(31) D. L. Lichtenberger and R. F. Fenske, *J. Am. Chem. Soc.*, **98**, 50 (1976).
(32) R. F. Fenske, *Pure Appl. Chem.*, **27**, 61 (1971).
(33) For a review, see R. F. Fenske, *Prog. Inorg. Chem.*, **21** 179 (1976).
(34) J. L. DeBoer, D. Rogers, A. C. Skapski, and P. G. H. Troughton, *Chem. Commun.*, **20**, 756 (1966).
(35) A. F. Berndt and R. E. Marsh, *Acta Crystallogr.*, **16**, 118 (1963).
(36) T. H. Whitesides, D. L. Lichtenberger, and R. A. Budnik, *Inorg. Chem.*, **14**, 68 (1975).
(37) E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965).
(38) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 768 (1972).
(39) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).
(40) D. L. Lichtenberger and R. F. Fenske, *J. Chem. Phys.*, in press.
(41) J. W. Rabalais, L. O. Werme, T. Bergmark, L. Karlsson, M. Hussain, and K. Siegbahn, *J. Chem. Phys.*, **57**, 1185 (1972).
(42) R. K. Nesbet, *J. Chem. Phys.*, **40**, 3619 (1964).
(43) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1970.
(44) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, London, 1969.
(45) T. Koopmans, *Physica*, **1**, 104 (1934).
(46) W. G. Richards, *Int. J. Mass. Spectrom. Ion Phys.*, **2**, 419 (1969).
(47) M. Coutiere, J. Demuynck, and A. Veillard, *Theor. Chim. Acta.*, **27**, 281 (1972).
(48) F. Brogli, P. A. Clark, E. Heilbronner, and M. Neuenschwander, *Angew. Chem., Int. Ed. Engl.*, **12**, 422 (1973).
(49) M. B. Hall, *J. Am. Chem. Soc.*, **97**, 2057 (1975).
(50) S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard, and C. F. Pygall, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1847 (1972).
(51) A. Schweig and W. Thiel, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 27 (1974).
(52) A. Katrib, T. P. Debies, R. J. Colton, T. H. Lee, and J. W. Rabalais, *Chem. Phys. Lett.*, **22**, 196 (1973).
(53) (a) K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *J. Chem. Phys.*, **22**, 1433 (1954); (b) G. Klopman and R. F. Hudson, *Theor. Chim. Acta*, **8**, 165 (1967); (c) T. F. Block, R. F. Fenske, and C. P. Casey, *J. Am. Chem. Soc.*, **98**, 441 (1976).
(54) I. S. Butler, private communication.
(55) J. Hoeft, F. J. Lovas, E. Tiemann, and T. Törring, *J. Chem. Phys.*, **53**, 2736 (1970).
(56) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **98**, 4110 (1976).

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Photochemistry and Photoisomerization of Five- and Six-Coordinate d^6 Transition Metal Thiocarbonyl Complexes in Low-Temperature Matrices

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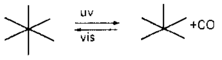
Uv photolysis (λ 300 ± 10 nm) of $M(CO)_5CS$ ($M = Cr$ or W) in Ar or CH_4 matrices at 20 K produces a mixture of two isomeric forms of $M(CO)_4CS$ and molecular CO. There is no evidence for loss of CS under these conditions. The relative yield of the two isomers depends both on the photolysis time and the matrix material. Quantitative analysis of band positions of the ir spectra of the ^{13}CO-enriched compounds and qualitative analysis of the band intensities show that both isomers have square-pyramidal structures: one has C_{4v} symmetry with the CS group in the axial position, and the other C_s symmetry with a basal CS group. Both isomers have visible absorption bands (for $Cr(CO)_4CS$/Ar λ_{max} C_{4v} 525 nm and C_s 562 nm). Irradiation with visible light of wavelength corresponding to the tail of the absorption band of one form of $M(CO)_4CS$ isomerizes it into the other form. Longer periods of irradiation with unfiltered visible light regenerates the parent $M(CO)_5CS$ molecule. Polarized photochemistry is used to assign the symmetries of the irradiated bands, and full uv–visible data are reported.

Introduction

Matrix isolation has already had considerable success in elucidating the structures of unstable transition metal carbonyl species.[1] The photolysis of the d^6 hexacarbonyl compounds, $M(CO)_6$ ($M = Cr$, Mo, and W), has produced particularly interesting results.[2-4] On irradiation with uv light, the octahedral $M(CO)_6$ molecule loses carbon monoxide to form a square-pyramidal $M(CO)_5$ fragment.[3] This pentacarbonyl has a visible absorption band, the exact position of which depends on both the metal and the matrix material.[4] Most surprisingly, irradiation of $M(CO)_5$ with light, corresponding to the wavelength of this absorption, regenerates the hexacarbonyl, $M(CO)_6$.



We have investigated the photochemistry of the analogous pentacarbonyl thiocarbonyl molecules, $M(CO)_5CS$ ($M = Cr$

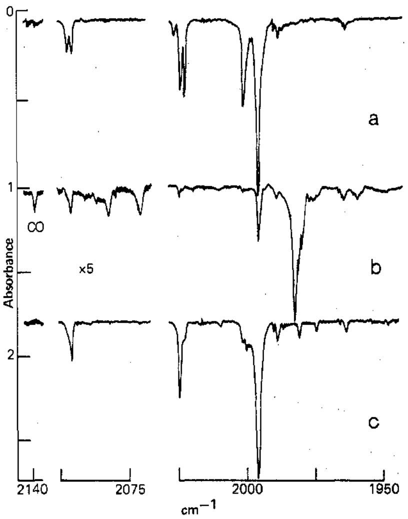
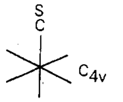


Figure 1. Ir spectra of $Cr(CO)_5CS$ in an Ar matrix (dilution 1:2000): (a) after deposition; (b) 115 min photolysis with λ 302 ± 10 nm, showing the growth of product bands and free CO (note the ordinate expansion above 2070 cm^{-1}); (c) 10 min photolysis with filtered Hg arc, λ >375 nm, showing the regeneration of the $Cr(CO)_5CS$ and disappearance of the product bands.

and W), which were originally prepared by Angelici and Dombek.[5] The study was started in the hope that the photochemistry of $M(CO)_5CS$ would be similar to that of $M(CO)_6$, and that the CS group could be used as a label to help elucidate reaction mechanisms. The experiments have proved highly successful and in this paper we report the structures of the primary photoproducts. In a subsequent paper[6] we show how stereospecific isotopic labeling has indeed provided detailed evidence of the photolysis mechanism.

Results and Discussion

Photolysis of $Cr(CO)_5CS$. Figure 1a shows the "C–O stretching" region of the ir spectrum of $Cr(CO)_5CS$, isolated in an Ar matrix at 20 K. Three normal C–O stretching modes (2 a_1 + e) and one C–S stretching mode (a_1) are predicted for $Cr(CO)_5CS$ (**1**). Although more than three C–O stretching bands are observed, these bands are clustered together into three groups. Each group is interpreted as being the *same* mode of molecules trapped in *different* sites in the matrix. The C–S mode, which is not illustrated in Figure 1, was also split into several bands. This "matrix splitting" of bands occurs with most transition carbonyls and has been discussed at length elsewhere.[2,7,8]



(1)

Irradiation of the matrix with a monochromated medium pressure mercury arc (see Experimental Section), λ 302 ± 10 nm for 115 min, destroyed most of the $Cr(CO)_5CS$ (Figure 1b). New ir bands appeared: an intense band at 1983 cm^{-1} and several weaker ones, including, in particular, molecular CO, at 2138 cm^{-1}. There were corresponding changes in the C–S region (1250–1300 cm^{-1}) but with this amount of $Cr(CO)_5CS$ deposited in the matrix the bands were too weak for detailed analysis. After irradiation for 10 min with the visible output of the mercury arc, λ >375 nm, the product bands, including the molecular CO, almost totally disappeared and the parent $Cr(CO)_5CS$ was regenerated, *but with all the bands unsplit*, Figure 1c. A similar disappearance of matrix splittings was reported for $M(CO)_6$, where it was attributed to a local annealing of the matrix.[2,3] Whatever its cause, this disappearance of the splittings is of considerable importance in the analysis of the spectra (see below). Thus, the first experiment has shown that the photochemistry of $Cr(CO)_5CS$ is superficially similar to that of $Cr(CO)_6$.

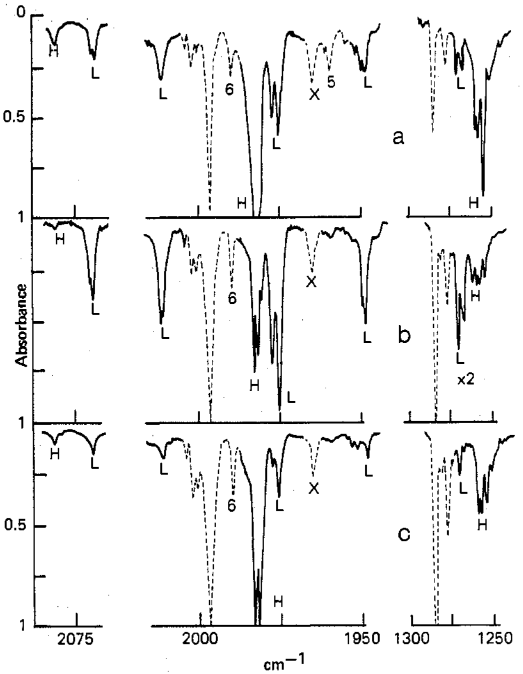


Figure 2. Ir spectra of $Cr(CO)_5CS$ in a thick Ar matrix (1:2000). Note that the C–S stretching region, 1250–1300 cm^{-1}, has ×2 ordinate expansion and ×$^1/_2$ abscissa expansion relative to the rest of the diagram: (a) 1100 min photolysis with 297 ± 10 nm, showing bands due to the two isomers of $Cr(CO)_4CS$ (H and L), $Cr(CO)_5CS$ (broken lines), $Cr(CO)_6$ (6), $Cr(CO)_5$ (5), and an uncharacterized secondary photolysis product (X); (b) 5 min photolysis, tungsten lamp with λ 489 nm filter, showing the growth of the bands marked L; (c) 5 min photolysis, tungsten lamp with λ 618 nm filter, showing regeneration of the bands H.

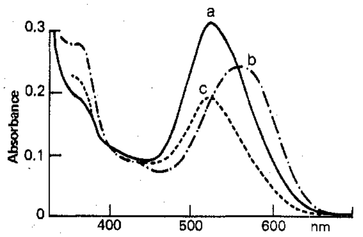


Figure 3. Uv–visible absorption spectra corresponding to the ir spectra in Figure 2, and taken at the same stages of the experiment using the same sample.

$$Cr(CO)_5CS \underset{visible}{\overset{uv}{\rightleftharpoons}} products + CO$$

The next experiment, however, indicates that the system is rather more complicated.

Figure 2a shows the ir spectrum obtained by 1100 min photolysis with λ 297 ± 10 nm of an Ar matrix, which contains the same concentration of $Cr(CO)_5CS$ (1:2000) as in Figure 1 but which is considerably thicker. Figure 3a shows the corresponding uv–visible spectrum of the *same* matrix. Figure 2 includes the C–S stretching region but two of the parent $Cr(CO)_5CS$ C–O stretching bands, 2095 and 2025.5 cm^{-1}, lie outside the wavenumber ranges of the figure. The remaining bands of $Cr(CO)_5CS$ are shown as dotted lines. The bands of the primary photochemical products fall into two groups, which have been labeled H and L. (Why the letters H and L were chosen will be explained later.) The reason for grouping the bands in this way becomes clear from Figures 2b and 2c. Irradiation of the matrix with a tungsten lamp and

Table I. Wavenumbers of $Cr(CO)_5CS$ and Its Photolysis Products in an Ar Matrix (Figures 1 and 2)

	Assignment		Assignment
		$Cr(CO)_5CS$	
2096.9		1285.8	
2095.0[a]	a_1	1284.7[a]	a_1 ν_{C-S}
2028.3[b]		1277.9[a]	
2025.5[a]	a_1	2088.1[b]	
2024		2018.2[b]	$Cr(CO)_4(^{13}CO)CS$[c]
2002.2		1965.2[b]	
1996.7[a]	e	1276.0[b]	
		1270.7[b]	$Cr(CO)_5(C^{34}S)$[c]
		H Isomer, $Cr(CO)_4CS$	
2085.3[b]		1260.2	
2081.3	a_1	1257.8	
1983.3		1254.9	a_1 ν_{CS}
1982.3	e	1253.7	
1980.9[b]		1250.6	
		L isomer, $Cr(CO)_4CS$	
2070.4[b]		1949.3	a′
2069.3	a′	1271	
2011.3	a′	1268	a′ ν_{C-S}
1977.7			
1975.6	a″		

[a] Bands which are regenerated by visible irradiation ($\lambda > 375$ nm). [b] Weak bands. [c] Natural abundance.

narrow band interference filter, λ 489 nm, for 5 min, causes the bands labeled H to decrease in intensity and those labeled L to substantially increase. At the same time, there has been a red shift in the λ_{max} of the visible absorption (Figure 3b). Irradiation for a further 5 min with the same lamp, but this time with a λ 618 nm filter, destroys the L bands and regenerates the H bands (Figure 2c) and shifts λ_{max} of the visible band back to its original value (Figure 3c). Both of these irradiations cause some regeneration of the parent $Cr(CO)_5CS$ bands. Thus, there appear to be at least two species, H and L, which are produced by uv photolysis of $Cr(CO)_5CS$, and their behavior can be summarized as:

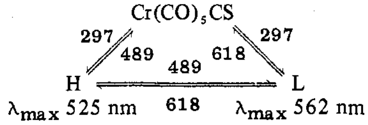
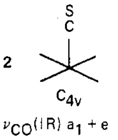


Figure 2 contains three other C–O stretching bands which have not yet been mentioned. They are a band labeled 6, which is due to traces of $Cr(CO)_6$ in the sample of $Cr(CO)_5CS$, and its photolysis product $Cr(CO)_5$, labeled 5, which is destroyed by the 489 nm light.

The third band is an uncharacterized secondary photolysis product, labeled X, which remains unchanged during the visible photolysis.

The wavenumbers of the ir bands are given in Table I. Allowing for "matrix splittings", the table suggests that H has two C–O and one C–S stretching modes, while L has four C–O and one C–S stretching modes. Since free CO is produced by the photolysis of $Cr(CO)_5CS$, H and L are probably different isomers of $Cr(CO)_4CS$. This would also explain their easy photochemical interconversion. What are their structures? There are four simple structures, C_{4v}, C_s, C_{2v}, and C_{3v}, which might be expected for $Cr(CO)_4CS$. The C_{4v} and C_s isomers are formally derived from square-pyramidal (SPY) $Cr(CO)_5$, and the C_{2v} and C_{3v} structures are derived from the much disputed[9,10] trigonal-bipyramidal (TBP) $Cr(CO)_5$. The number of CO stretching modes suggests that H (two modes) is the C_{4v} isomer (**2**). L has four distinct modes, which are too widely separated to be the split bands of the C_{3v} isomer (**5**) (only three modes), and is most probably either the C_s (**3**) or C_{2v} (**4**) isomer, both of which have four modes. Hence the choice of the letters: H for the *high*-symmetry isomer and L for the *low*-symmetry isomer. We have used ^{13}CO enrichment to distinguish between these two possible structures of L and to confirm the structure of H.

2



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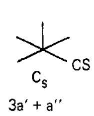

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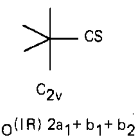


5

Structure Determination Using ^{13}CO Enrichment. The use of isotopic CO for determining the structures of metal carbonyls has been extensively discussed elsewhere.[3,11-13] Essentially the ir spectrum is recorded for a sample of the carbonyl which has been enriched with ~50% ^{13}CO and the observed spectrum is compared with the spectra predicted for the various possible structures. It is important for the method that the ^{13}CO should be distributed statistically among all the possible $M(^{12}CO)_{n-x}(^{13}CO)_x$ molecules. The calculations use a CO-factored force field, which means that they neglect all **G** and **F** matrix coupling between the C–O stretching modes and the other vibrations of the carbonyl molecule. The **G** matrix coupling between the CO groups themselves is also zero since the groups have no atoms in common. The majority of previous calculations have used unsubstituted metal carbonyls (e.g., $M(CO)_6$[3]) and it was important to see whether coupling between the C–O and C–S stretching vibrations could be neglected in the $M(CO)_nCS$ species. Thus we decided to analyze the spectrum of ^{13}CO enriched $Cr(CO)_5CS$ before drawing structural conclusions about the $Cr(CO)_4CS$ fragments from their spectra.

Figure 4a shows the ir spectrum in the C–O stretching region of $Cr(CO)_5CS$ with 57% ^{13}CO enrichment. (Throughout Figure 4, bands not assignable to the compound under consideration are drawn in dotted lines.) The spectrum was obtained by uv photolysis of $Cr(CO)_5CS$, followed by irradiation of the products with visible light to regenerate the $Cr(CO)_5CS$. This procedure removed the matrix splittings from the bands (see Figure 1). The C–S stretching region is not shown in Figure 4 as the bands were identical in position and half-width to those of the unenriched compounds. Figure 4b shows the computer-drawn spectrum predicted for C_{4v} $Cr(CO)_5CS$, neglecting all interaction with the CS group. Details of the calculations are given in an Appendix to this paper, the force constants are defined in Figure 5a, and the observed and calculated frequencies are shown in Table II. It is striking that not only does the calculation give an excellent fit of the observed band positions,[14] but also reproduces nearly all the features of the observed spectrum. The sole exception is the small peak on the right-hand side of the strong band at 1950 cm^{-1}, which is assigned to a matrix splitting. It should be pointed out that the calculations assume a constant line width of 0.8 cm^{-1} for all the bands and this makes the calculated high-frequency bands (2100–2050 cm^{-1}) appear somewhat taller and thinner than in the observed spectrum. However, it is clear that the C–O stretching region of the spectrum can be successfully analyzed without including coupling with the C–S vibrations.

Uv photolysis of the ^{13}CO enriched $Cr(CO)_5CS$ produced a large number of new ir bands. These could be assigned to one of the two isomers, H or L, by use of 489 and 618 nm photolysis (cf. Figure 2). Figure 4c shows the bands assigned

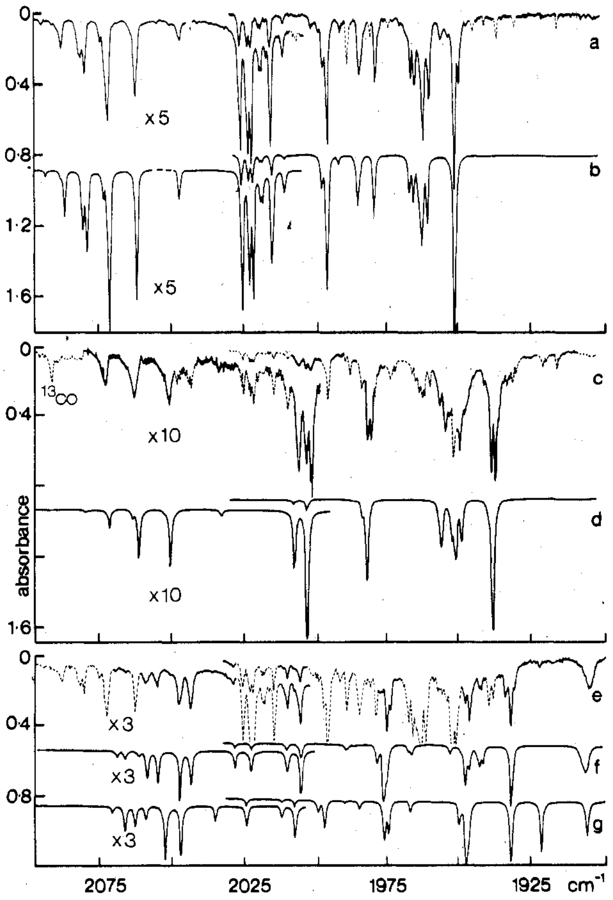


Figure 4. Observed and predicted ir spectra for $Cr(^{12}CO)_{n-x}(^{13}CO)_xCS$ species with 57% ^{13}CO enrichment. Details of the calculations used to predict the spectra are given in the Appendix. In each observed spectrum bands not assigned to the compound under consideration are shown in broken lines. (a) Spectrum of $Cr(CO)_5CS$ after regeneration with visible light to remove matrix splittings (cf. Figure 1). (b) Predicted spectrum for C_{4v} $M(CO)_5$ unit with no CO–CS coupling, and 0.8 cm^{-1} line width. (c) Bands assigned to the high-symmetry isomer (H) of $Cr(CO)_4CS$, obtained by 1180 min photolysis with λ 300 ± 10 nm. (d) Predicted spectrum for C_{4v} $M(CO)_4$ unit, 1 cm^{-1} line width. (e) Bands assigned to the low-symmetry isomer, L, of $Cr(CO)_4CS$, obtained by 13 min irradiation of (c) with tungsten lamp plus λ 489 nm filter. (e) Predicted spectrum for a C_s $M(CO)_4$ unit, 1 cm^{-1} line width. (f) Predicted spectrum for a C_{2v} $M(CO)_4$ unit, 1 cm^{-1} line width. (Note that the low-frequency portion of spectrum a and the high-frequency part of spectrum c were taken from a separate experiment but using the same sample ^{13}CO enriched $Cr(CO)_5CS$.)

to isomer H, and Figure 4d shows the spectrum predicted for C_{4v} $Cr(CO)_4CS$. The force constants are defined in Figure 5c and the frequencies are given in Table III. In this case, the detailed pattern of the spectrum is not reproduced as well as that of $Cr(CO)_5CS$, because many of the principal bands are split. Nevertheless, the overall pattern is predicted most successfully and there are no bands observed in places where none are predicted or vice versa. This suggests most strongly that H is indeed the C_{4v} SPY $Cr(CO)_4CS$ (**2**).

The spectrum of the isomer L is shown in Figure 4e and the frequencies are given in Table IV. On the basis of the number of CO stretching modes L could have either the C_s SPY **3** or the C_{2v} TBP **4** structure (qv). We have previously analyzed C_{2v} tetracarbonyls, e.g., $Fe(CO)_4$[12] or $Mo(CO)_4$,[4] but this is the first case of a C_s tetracarbonyl being treated in this way. The force constants are therefore defined in Figures 5e, C_s, and 5g, C_{2v}, and the 12 possible ^{13}CO substituted C_s $M(CO)_4$ molecules are enumerated in Figure 6.

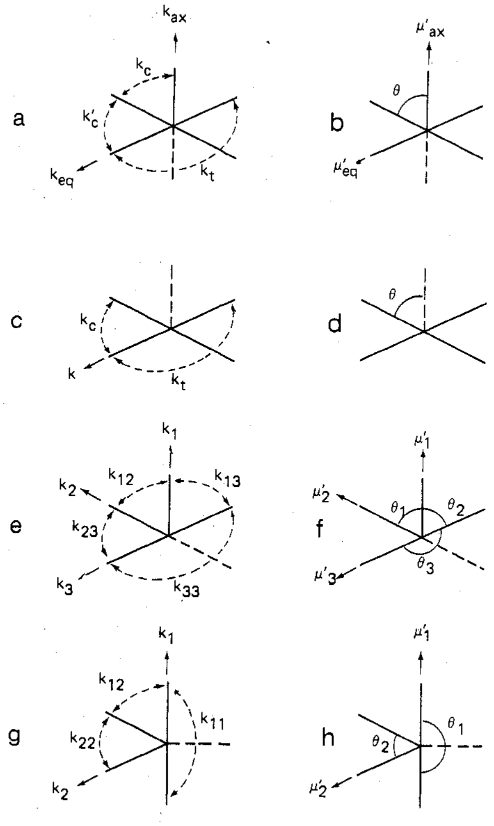


Figure 5. Definition of force constants (a, c, e, g) and bond angles and dipole moment derivatives (b, d, f, h) for $Cr(CO)_5CS$ (a, b), C_{4v} $Cr(CO)_4CS$ (c, d), C_s $Cr(CO)_4CS$ (e, f), and C_{2v} $Cr(CO)_4CS$ (g, h). See Figure 4 and the Appendix. The broken line represents the CS group.

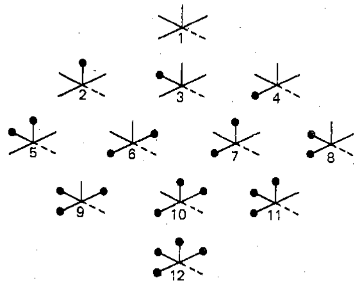


Figure 6. C_s $M(^{12}CO)_4CS$ (**1**) and the 11 possible ^{13}CO-substituted molecules (**2–12**). The black circle represents ^{13}CO and the broken line the CS group. Molecules 4, 7, 8, and 11 have C_1 symmetry and all others C_s symmetry.

As before details of all calculations are given in the Appendix. The spectra calculated for the two structures are shown in Figure 4, C_s SPY, spectrum f, and C_{2v} TBP, spectrum g. Comparison of these two spectra with the observed spectrum e shows that the C_s SPY structure **3** predicts the observed bands much better than the C_{2v} TBP structure **4**. The following points should be noted in particular: (1) The C_{2v} structure predicts several intense bands which are not observed, e.g., 2053 and 1921 cm^{-1}, etc., while the C_s structure does not. (2) The broad (~1905 cm^{-1}) band on the extreme right of spectrum e is predicted by the C_{2v} structure to be sharp but by the C_s structure to be broad since it is the envelope of several overlapping sharp bands. (3) Because of the poor agreement between the observed spectrum and the C_{2v} prediction it was not possible to refine the force constants and an approximate force field had to be used. However, the approximation used (see Appendix) has proved highly successful with $Fe(CO)_4$[12] and $Mo(CO)_4$[4] where all the bands

Table II. Observed and Calculated Wavenumbers[e] for $Cr(CO)_5CS$ in an Ar matrix

Molecule	Symmetry	Obsd	Calcd[d]
$Cr(^{12}CO)_5CS$	a_1	2095.0	2094.4
C_{4v}	a_1	2025.5	2025.3
	b_2	*a*	2024.9
	e	1996.9	1996.7
$Cr(^{12}CO)_4(^{13}CO)CS$	a_1	*b*	2089.2
C_{4v}	a_1	*c*	1985.1
	b_2	*a*	2024.9
	e	1996.9	1996.7
$Cr(^{12}CO)_4(^{13}CO)CS$	a′	2088.2	2087.9
C_s	a′	*c*	2025.2
	a′	2018.1	2018.0
	a′	1965.2	1965.1
	a′	1996.9	1996.7
$Cr(^{12}CO)_3(^{13}CO)_2CS$	a′	2081.9	2081.8
C_s(ax eq)	a′	2019.1	2018.8
	a′	1985.8	1985.8
	a′	*c*	1964.4
	a″	1996.9	1996.7
$Cr(^{12}CO)_3(^{13}CO)_2CS$	a′	2080.3	2080.1
C_s(eq eq)	a′	2022.9	2022.8
	a′	1967.8	1968.1
	a″	2015.1	2014.7
	a″	1961.8	1962.0
$Cr(^{12}CO)_3(^{13}CO)_2CS$	a_1	*c*	2081.4
C_{2v}	a_1	*c*	2025.2
	a_1	1992.1	1992.1
	b_1	1996.9	1996.7
	b_2	1952.7	1952.2
$Cr(^{12}CO)_2(^{13}CO)_3CS$	a′	*c*	2072.3
C_s(ax eq)	a′	2021.8	2021.4
	a′	*c*	1992.7
	a′	*c*	1963.9
	a″	1952.7	1952.2
$Cr(^{12}CO)_2(^{13}CO)_3CS$	a′	2072.1	2072.6
C_s(eq eq)	a′	*c*	1986.3
	a′	1966.4	1966.7
	a″	2015.1	2014.7
	a″	1961.8	1962.0
$Cr(^{12}CO)_2(^{13}CO)_3CS$	a_1	2074.9	2074.4
C_{2v}	a_1	*c*	1998.9
	a_1	*c*	1980.1
	b_1	1952.7	1952.2
	b_2	1996.9	1996.7
$Cr(^{12}CO)(^{13}CO)_4CS$	a_1	*c*	2062.9
C_{4v}	a_1	2010.5	2010.5
	b_2	*a*	1979.7
	e	1952.7	1952.2
$Cr(^{12}CO)(^{13}CO)_4CS$	a′	2062.5	2062.8
C_s	a′	1998.1	1998.4
	a′	1979.8	1980.1
	a′	1963.6	1963.7
	a″	1952.7	1952.2
$Cr(^{13}CO)_5CS$	a_1	2047.0	2047.8
C_{4v}	a_1	*c*	1980.2
	b_2	*a*	1979.7
	e	1952.7	1952.2

[a] Ir inactive. [b] Not observed. [c] Predicted to be obscured by other bands. [d] Force constants (see Figure 5a) $k_{ax} = 1677.56$, $k_{eq} = 16.5726$, $k_c = 22.026$, $k_{c'} = 23.821$, $k_t = 46.689$ N m^{-1}. [e] Standard deviation (26 frequencies) 0.35 cm^{-1}; maximum error 0.75 cm^{-1}.

were predicted within 2 or 3 cm^{-1}, and so the prediction should not be rejected on these grounds. Thus the observed spectrum is much better explained on the basis of a C_s SPY structure for L.

Evidence for Loss of CS. Under these photolysis conditions there seems to be no evidence for loss of the CS group. The bands of $M(CO)_5$ (e.g., Figure 2a) are due to photolysis of $M(CO)_6$ impurities and when these impurities were absent, no $M(CO)_5$ was observed. The uncharacterized product X (Figure 2) was not $Cr(CO)_4$,[4] and thus there is no evidence for CS loss by secondary photolysis of $M(CO)_4CS$.

Table III. Observed and Calculated Wavenumbers[f] for C_{4v} $Cr(CO)_4CS$ in an Ar Matrix

Molecule		Obsd		Calcd[e]
$Cr(^{12}CO)_4CS$	a_1	2081.4		2080.3
C_{4v}	b_2	*a*		2016.0
	e	1983.3 1982.3	1982.8[b]	1983.4
$Cr(^{12}CO)_3(^{13}CO)CS$	a′	2072.1		2072.3
C_s	a′	2010.1		2009.3
	a′	*c*		1953.1
	a″		1982.8[b]	1983.4
trans-$Cr(^{12}CO)_2(^{13}CO)_2CS$	a_1	2064		2064.5
C_{2v}	a_1	*c*		1986.2
	b_1		1982.8[b]	1983.4
	b_2		1939.3[b]	1939.2
cis-$Cr(^{12}CO)_2(^{13}CO)_2CS$	a′	2062.4		2062.2
C_s	a′	2004		2004.9
	a″	1956.5		1956.2
	a″	1950.4		1949.9
$Cr(^{12}CO)(^{13}CO)_3CS$	a′	2050.6		2051.4
C_s	a′	*c*		1985.7
	a′	*c*		1952.0
	a″		1939.3[b]	1939.2
$Cr(^{13}CO)_4CS$	a_1	*d*		2033.9
C_{4v}	b_2	*a*		1971.0
	e	1940.0 1938.6	1939.3[b]	1939.2

[a] Ir inactive. [b] Mean value entered in refinement (see Appendix). [c] Band predicted to be obscured by other bands. [d] Not observed. [e] Force constants (see Figure 5c) $k = 1642.10$, $k_c = 26.624$, $k_t = 52.923$ N m^{-1}. [f] Standard deviation (11 frequencies) 0.62 cm^{-1}; maximum error 1.1 cm^{-1}.

However, prolonged photolysis (~4 h) of $M(CO)_5CS$ in a pure CO matrix with an *unfiltered* Hg arc does result in the slow formation of $M(CO)_6$. In this matrix, loss of CO will be almost completely reversible, while loss of CS is likely to be irreversible.

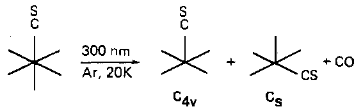
$$M(CO)_5CS \underset{\text{visible}}{\overset{\text{uv}}{\rightleftharpoons}} M(CO)_4CS + CO$$

$$M(CO)_5CS \xrightarrow{\text{uv}} M(CO)_5 + CS$$

$$M(CO)_5 + CO \xrightarrow{\text{visible}} M(CO)_6$$

Thus loss of the CS group, which is normally an insignificant process, becomes detectable. Using ^{13}CO labeled $W(CO)_5CS$, we have shown that CO exchange with the matrix is indeed many times faster than the formation of $W(CO)_6$. The analogous loss of NO from $Co(CO)_3NO$ in a pure CO matrix which was reported by us previously[15] has been explained by a similar mechanism.

Product Distribution and Uv Spectra. We are now in a position to summarize the uv photolysis of $Cr(CO)_5CS$. The



same results were found for $W(CO)_5CS$. There are two further questions of interest: first, were the two isomers of $M(CO)_4CS$ formed simultaneously or sequentially, and second, what were the relative amounts of the two isomers produced.

Analysis of the ir spectra taken at different stages during the photolysis shows that, initially, both isomers were formed together but as the photolysis proceeded the C_s isomer reached a steady state concentration and finally decreased. The reason for this lies in the uv spectra of $M(CO)_5CS$ and the two $M(CO)_4CS$ isomers. Figure 7a illustrates the spectrum of $W(CO)_5(CS)$ in a CH_4 matrix. There are three strong bands and four weaker bands, at least two with vibrational fine

Table IV. Observed and Calculated Wavenumbers[c] for C_s $Cr(CO)_4CS$ in an Ar Matrix (The Numbering of the Molecules Refers to Figure 6)

Molecule		Obsd	Calcd[b]
$Cr(^{12}CO)_4CS$ (**1**)	a′	2069.3	2069.1
	a′	2011.3	2011.2
	a′	1949.3	1949.3
	a″	1975.6	1976.1
$Cr(^{12}CO)_3(^{13}CO)CS$ (**2**)	a′	2065.6	2066.3
	a′	*a*	2011
	a′	*a*	1908.7
	a″	1975.6	1976.1
$Cr(^{12}CO)_3(^{13}CO)CS$ (**3**)	a′	*a*	2061.6
	a′	*a*	1979.1
	a′	*a*	1943.8
	a″	1975.6	1976.1
$Cr(^{12}CO)_3(^{13}CO)CS$ (**4**)		2058.9	2058.5
		2006.5	2006.6
		a	1953.1
		a	1942.8
$Cr(^{12}CO)_2(^{13}CO)_2CS$ (**5**)	a′	*a*	2058.9
	a′	*a*	1975.1
	a′	1906.3	1906.9
	a″	1975.6	1976.1
$Cr(^{12}CO)_2(^{13}CO)_2CS$ (**6**)	a′	2047.6	2047.6
	a′	*a*	1990.0
	a′	*a*	1946.4
	a″	1932.4	1932.1
$Cr(^{12}CO)_2(^{13}CO)_2CS$ (**7**)		2055.0	2055.2
		a	2006.5
		1948.0	1947.7
		a	1907.8
$Cr(^{12}CO)_2(^{13}CO)_2CS$ (**8**)		*a*	2047.7
		a	1978.7
		a	1947.8
		1942.5	1941.6
$Cr(^{12}CO)(^{13}CO)_3CS$ (**9**)	a′	2029.1	2028.7
	a′	*a*	1966.4
	a′	*a*	1905.9
	a″	1932.4	1932.1
$Cr(^{12}CO)(^{13}CO)_3CS$ (**10**)	a′	2043.4	2043.7
	a′	*a*	1989.3
	a′	*a*	1907.4
	a′	1932.4	1932.4
$Cr(^{12}CO)(^{13}CO)_3CS$ (**11**)		*a*	2044.2
		a	1975.2
		1946.5	1946.5
		a	1906.2
$Cr(^{13}CO)_nCS$ (**12**)	a′	*a*	2023.0
	a′	*a*	1966.4
	a′	*a*	1905.9
	a″	1932.4	1932.1

[a] Bands predicted to be obscured by other bands. [b] Force constants (see Figure 5e) $k_1 = 1552.12$, $k_2 = 1653.61$, $k_3 = 1635.19$, $k_{12} = 36.638$, $k_{13} = 28.327$, $k_{23} = 24.845$, and $k_{33} = 57.671$ N m^{-1}. [c] Standard deviation (16 frequencies) 0.4 cm^{-1}; maximum error 0.86 cm^{-1}.

structure. This fine structure is similar to that observed for matrix isolated $W(CO)_6$[8] (see Table V). The spectrum of $Cr(CO)_5CS$ has bands in positions close to those of $W(CO)_5CS$ but the band at 300.5 nm is somewhat stronger relative to the others, and the fine structure is absent (Table V). The spectra of the C_s isomer (solid line) and C_{4v} isomer (broken line) of $W(CO)_4CS$ are shown in Figure 7b. The band positions are given in Table V. In these experiments the photolysis wavelength was 300 ± 10 nm. Initially the light will be absorbed by the 304-nm band of $W(CO)_5CS$, but as the photolysis continues the C_s isomer which has a band at 283.5 nm will absorb progressively more light. This causes the C_s isomer to isomerize to the C_{4v} form which has no strong absorptions in the region of the photolysis wavelength. Irradiation in any band of one isomer causes isomerization to the other. For $W(CO)_4CS$ in a CH_4 matrix there is an isobestic point between the two isomers at 268 nm.

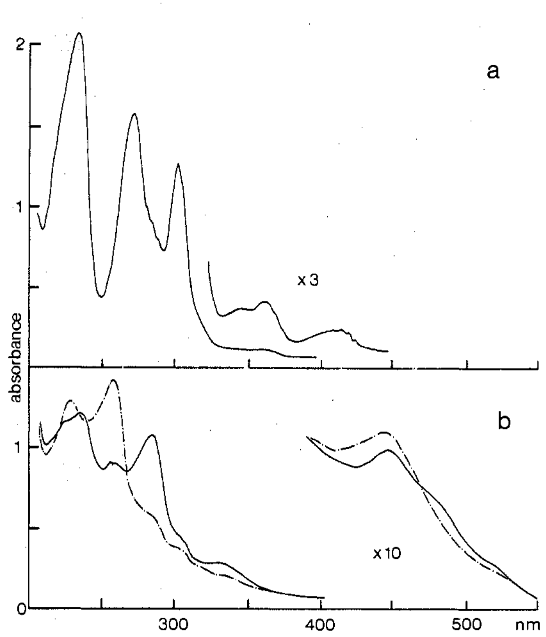


Figure 7. Uv-visible spectra of $W(CO)_nCS$ species in a CH_4 matrix (1:15 000) at 20 K. (a) $W(CO)_5CS$ before photolysis. The sample contains 5-10% $W(CO)_6$. The expanded part of the spectrum was taken from a separate experiment. (b) Spectra of the isomers of $W(CO)_4CS$. Solid line, sample containing principally C_s $W(CO)_4CS$. Broken line, sample containing principally the C_{4v} isomer, obtained by photolysis of C_s isomer with visible (5 min, 489 nm) and uv (60 min, 270 nm) light. All spectra from the same experiment.

Table V. Uv-Visible Absorption Maxima (nm) of $M(CO)_5CS$, $M(CO)_4CS$, $M(CO)_6$, and $M(CO)_5$ Species in Ar and CH_4 Matrices

$Cr(CO)_5CS$	$W(CO)_5CS$		$W(CO)_6$[a]
Ar	Ar	CH_4	CH_4
230.5	232.5	234.5	225
268	270	273.5	
	284[b] (550)[c]	286.5[b] (490)[c]	268[b] (550)[c]
300.5	301.5	304.5	295
	341[b]	346[b]	309[b] (450)[c]
362[b]	360[b]	367[b]	345[b] (430)[c]
394[b]	413[b] (270)[c]	416[b] (270)[c]	

$Cr(CO)_4CS$	$W(CO)_4CS$		$W(CO)_5$[e]
C_{4v}/Ar	C_{4v}/Ar	C_{4v}/CH	CH_4
		227	
241	256	257.5	244
525	474	445	413

$Cr(CO)_4CS$	$W(CO)_4CS$	
C_s/Ar	C_s/Ar	C_s/CH_4
		238
264	283	283.5
		335[b]
562	481[b,d]	470[b,d]

[a] Reference 8. [b] Weak bands. [c] Spacing of vibrational fine structure in cm^{-1}. [d] Positions only approximate because of band overlap. [e] Reference 4.

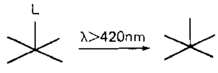
An interesting feature of the $M(CO)_5$ fragments, generated by photolysis of $M(CO)_6$, was the variation in position of the visible absorption band from one matrix to another.[4,8] For example, the absorption maximum for $W(CO)_5$ changed from 437 nm in an Ar matrix to 413 nm in CH_4. This shift of ~1330 cm^{-1} has been shown to be caused by a stereospecific $M(CO)_5$⋯matrix interaction which is stronger for CH_4 than argon.[4,8] An almost identical shift, ~1375 cm^{-1}, from 474 nm (Ar) to 445 nm (CH_4) was observed for C_{4v} $W(CO)_4CS$, with a somewhat smaller shift (~500 cm^{-1}) for the C_s isomer. These shifts, presumably also due to matrix···carbonyl interactions, serve to underline the similarities between the two $M(CO)_4CS$ isomers and $M(CO)_5$.

The relative amounts of C_{4v} and C_s isomers produced on initial photolysis can be deduced approximately from the relative intensities of the e band of the C_{4v} isomer (~1983 cm^{-1} for Cr/Ar) and the a″ band (~1976 cm^{-1}) of the C_s isomer. On a simple model[3,13] the extinction coefficient of the e mode should be twice that of the a″. In an argon matrix the e band is approximately four times as intense as the a″ band and thus there is twice as much C_{4v} isomer as C_s. For $Cr(CO)_5CS$ in a CH_4 matrix the intensities are almost equal, which suggests half as much C_{4v} as C_s. It is clear therefore that the ratio is matrix dependent. However, in an Ar matrix there is much more C_{4v} than C_s even after very short photolysis times when the chances of secondary photolysis of the C_s isomer were small.

Photolysis Using Linealy Polarized Light. We have recently demonstrated how polarized light can be used to generate oriented samples of matrix isolated carbonyls.[16] Irradiation of $W(CO)_5CS$ and $Cr(CO)_5CS$ in Ar and CH_4 matrices with polarized light (λ 300 ± 10 or 270 ± 10 nm) left oriented samples of unreacted $M(CO)_5CS$ but there was substantially less orientation of the products, $M(CO)_4CS$. This strongly suggests that an $M(CO)_4CS$ fragment must rotate in the matrix relative to the $M(CO)_5CS$ molecule from which it is generated. The ir linear dichroism confirmed that the two bands of $M(CO)_5CS$ assigned to a_1 modes had a different symmetry from the band assigned to the e mode. Comparison of the ir and uv polarizer directions showed that the photochemically active uv transition had overall a_1 symmetry. That is that the photochemistry must originate at least in part from the population of an A_1 excited state.[17]

Oriented samples of both isomers of $Cr(CO)_4CS$ should be produced by photolysis with polarized visible light of the appropriate wavelength. The results showed that the visible band of the C_{4v} isomer had e symmetry, which is the same as the corresponding band of $Cr(CO)_5$, and is consistent with an $b^2{}_2e^3a^1{}_1 \leftarrow b^2{}_2e^4$ transition. For the C_s isomer, the visible band had a polarization which was the same as that of the a″ C–O vibration and the opposite of the polarization of the lowest frequency a′ mode. The a″ mode has a dipole moment change in the basal plane of the square pyramid and the a′ mode principally involves the vibration of the "axial" CO group. Thus the transitions of both isomers of $Cr(CO)_4CS$ involve dipole moment changes in the basal plane of the square pyramid.

Mechanism of Isomerization of $M(CO)_4CS$. The mechanism of this isomerization induced by visible light is obviously closely related to the regeneration of $M(CO)_5CS$, since both processes involve irradiation of the same absorption band. The mechanisms of these reactions, and the regeneration of $M(CO)_6$ from $M(CO)_5$, will be discussed in detail elsewhere.[18] However, there are several points that should be made at this stage. (1) The isomerization is similar to the reaction reported by Black and Braterman[19] for $Mo(CO)_4L$, where L = P-(cyclohexyl)$_3$ in hydrocarbon glass at 77 K, although in that case the process was only observed in one direction. (2) The fact that the isomerization could be observed at all means that the quantum yield for the isomerization must be substantially higher than the quantum yield for the regeneration of $M(CO)_5CS$. It is interesting to note that the quantum yield for the regeneration of $Mo(CO)_6$ from $Mo(CO)_5$ in both Ar and CH_4 matrices was substantially less than unity.[20] Photolysis of stereospecifically ^{13}CO enriched $M(CO)_5CS$ suggests that the quantum yield for the $C_s \rightarrow C_{4v}$ isomerization is also less than unity.[6] (3) The extremes of isomerization illustrated in Figures 2b and 2c represent photostationary states, dictated by the relative extinction coefficients of the two isomers, rather than any thermodynamic equilibria. Any mixture of the two isomers appears to be stable indefinitely, once the light source has been removed, which shows that at 20 K the molecules do not undergo any thermal fluxional rearrangements resulting in isomerization. Experiments described in a subsequent paper[6] also eliminate continuous thermal rearrangements, which permute CO groups without isomerization. (4) Since the isomers are not fluxional in the ground state, it follows that the photochemical isomerization must occur in a low electronic excited state or a vibrationally excited ground state. (5) The isomerization requires substantial movement of at least one ligand relative to the matrix cage. If a similar rearangement process were to occurr on irradiation of $M(CO)_5$, where of course it would not be directly observable, it would provide a mechanism[18] for the photoreorientation[16] of $Cr(CO)_5$.



Experimental Section

Samples of $Cr(CO)_5CS$ and $W(CO)_5CS$ were gifts from Professor R. J. Angelici, who prepared them by his published methods,[5] and were used without further purification. ^{13}CO enrichment was achieved by photolysis for 1 h of a solution of 5 mg of $Cr(CO)_5CS$ in 1 ml of isopentane under atmosphere of 90% ^{13}CO (BOC Prochem), with constant shaking, using a focused high-pressure mercury arc filtered with Pyrex glass.[21] All matrix gases were "Grade X" gases as supplied by BOC Ltd. Gas phase mixtures of $Cr(CO)_5CS$ were found to decompose rapidly, ~2 h, while $W(CO)_5CS$ was more stable.

The matrix experiments were performed at 20 K using an Air Products Displex CS-202 closed-cycle Helium refrigerator. The apparatus has been described in detail previously.[7,22] Ir spectra were recorded using a Grubb Parsons Spectromajor spectrophotometer using gaseous DCl and DBr and CH_4 as calibrants. Wavenumbers of bands were measured by interpolation between bands of the calibrating gases using a Ferranti Freescan Digitizer. Band positions were reproducible to ±0.2 cm^{-1} and the spectrometer resolution was 0.4 cm^{-1} (i.e., the $D^{79}Br$ and $D^{81}Br$ vibration/rotation doublets were well resolved). All spectra were run with a polished germanium filter to remove any visible light from the spectrometer beam. Polarization experiments used a SpecAc aluminum grid polarizer on a KRS-5 substrate. Uv spectra were run on a Perkin-Elmer 356 spectrophotometer using holmium oxide glass calibration. Polacoat 105 UV WMR polarizers on quartz substrates were used.

The photolysis source was a Philips HPK-125W medium pressure Hg arc, which was focused with *f*/4 quartz optics onto the entrance slits of an Applied Photophysics M300 High Radiance monochromator. Analysis of the output beam using a McPherson 218 scanning monochromator suggested that the scattered light level was low. The visible photolysis source was a 100-W tungsten iodide projector lamp with a focusing dichroic reflector. The beam was filtered with a 4 cm quartz water cell and Balzers narrow band pass interference filters. The λ >375 nm filter was a Balzers Calfex C heat absorbing filter. Calculations were performed using a Hewlett Packard 2000-E time shared computer. The computed spectra were plotted using the IBM 360/67 and 370/169 computers of the Newcastle University Computing Laboratory.

Conclusion

It is clear that the photochemistry of the thiocarbonyl complexes, $M(CO)_5CS$, mirrors that of the hexacarbonyl molecules, $M(CO)_6$. On uv photolysis, both species lose CO to form five-coordinate square-pyramidal fragments, from which the parent carbonyl can be regenerated by irradiation with visible light. $M(CO)_4CS$ differs, of course, from $M(CO)_5$ in that it has two SPY isomers, but each of these exhibits a substantial shift in position of its visible absorption band on going from one matrix to another, in a manner similar to $M(CO)_5$.[4] In many of the reactions, therefore, the CS is

Table VI. Force Constants for $Cr(CO)_5CS$ in an Ar matrix ($N\ m^{-1}$)

	a	*b*	*c*
k_{ax}	1677.56	1677.97	1677.50
k_{eq}	1657.26	1657.91	1657.10
k_c	22.026	22.020	21.439
$k_{c'}$	23.821	23.860	23.634
k_t	46.869	46.423	46.487
$k_{cs}{}^d$	848.86	848.86	852.41
k_{cs-eq}	0	0	15.718
k_{cs-ax}	0	0	52.166
Standard deviation, cm^{-1}	0.35	0.25	0.36
Maximum error, cm^{-1}	0.75	0.63	0.8
$(\mu_{^{13}CO}/\mu_{^{12}CO})^{1/2}$	0.977 71	0.977 34 (ax) 0.977 37 (eq)	0.97771

[a] Fixed reduced masses, no C–S interaction. [b] Reduced mass ratios for axial and equatorial groups additional variables, no C–S interaction. [c] Fixed reduced masses, but including C–S interaction. [d] Using $\nu_{C^{32}S} = 1285\ cm^{-1}$.

behaving merely as a labeled CO group allowing one to follow otherwise unobservable processes. In a subsequent paper[6] we show how this labeling can be used to elucidate reaction pathways.

Acknowledgment. I thank the Science Research Council for supporting this research, Professor R. J. Angelici and Dr. B. D. Dombek for the gift of the thiocarbonyl complexes, Dr. W. Clegg for advice on computing, and Professor J. J. Turner and Drs. J. K. Burdett, I. R. Dunkin, and R. N. Perutz for their help.

Appendix

General Method of Calculation. This appendix gives details of the force constant calculations for the $Cr(CO)_5CS$ and $Cr(CO)_4CS$ species, using CO factored force fields. All force constants were refined using the "least-squares" method described by Perutz and Turner.[3] Each observed wavenumber was only entered once into the refinement. Band intensities of ^{13}CO substituted molecules were calculated using the eigenvectors of the unsymmetrized $\mathbf{G}^{1/2}\mathbf{F}\mathbf{G}^{1/2}$ matrix[3,11] and the bond angles and dipole moment derivative ratios, calculated from the band intensities of the unenriched molecule using previously reported methods.[3] This produced a "stick" spectrum, around which Lorentzian bandshapes of constant line width were constructed. The value used was an experimental line width (full width at half-height), measured from the spectrum for a band which did not significantly overlap with any others. The percentage ^{13}CO enrichment was calculated from the relative intensities of the bands at 1996.7 and 1952.7 cm^{-1}. All the force constants are quoted to a large number of significant figures to allow our calculations to be repeated.

Analysis of the Spectrum of $Cr(CO)_5CS$. (a) Band Assignment. The frequencies of the $Cr(^{12}CO)_5CS$ molecule were used to calculate the three "Cotton–Kraihanzel" force constants,[23] k_{ax}, k_{eq}, and k_i, where $k_i = k_c = k_{c'} = {}^1/_2k_t$ (see Figure 5a). The frequencies of all the possible $Cr(^{12}CO)_{5-x}(^{13}CO)_x$ CS molecules were then calculated using these approximate force constants. The agreement between the observed and calculated frequencies (0.51 cm^{-1} standard deviation) was sufficiently good to allow most of the observed bands to be assigned. The full least-squares refinement was then calculated in the usual manner.[3] The final force constants (0.35 cm^{-1} standard deviation) are given in Table VI column *a*.

(b) Ratio of the Reduced Masses of ^{13}CO and ^{12}CO. In the CO factored force field the vibrational frequencies of a molecule $M(^{12}CO)_x$ are related to those of $M(^{13}CO)_x$ by the ratio of the square roots of the reciprocal reduced masses, $(\mu_{^{13}CO}/\mu_{^{12}CO})^{1/2}$, which, using the appropriate isotopic masses, is 0.977 71. However, it can be seen from Table II that the ratios of the observed frequencies $Cr(^{13}CO)_5CS$ and $Cr(^{12}CO)_5CS$ are subsantially different from this, 0.977 10 ($a_{1,high}$) and 0.977 96 (e). Braterman[24] has recently carried out the vibrational analysis of a hypothetical linear MCO molecule using a force field which included both M–C and C–O vibrations, appropriate **G** and **F** matrix coupling, and estimated values of the force constants. He found a ratio $(\nu_{^{13}CO}/\nu_{^{12}CO}) = 0.977\,28$. The difference between his prediction and that of the CO factored force field is caused by the significant proportion of M–C stretching character in the so-called "C–O stretching" mode. Braterman therefore suggested[24] that his "effective" ratio (0.977 28) would be a better value to use in CO factored force field calculations than the ratio (0.977 71) derived from isotopic masses. The difference between the two ratios corresponds to a difference of 0.9 cm^{-1} in the isotopic shift predicted for a band of $M(^{12}CO)_x$ at 2000 cm^{-1}.

To test this proposal we allowed the reduced mass of ^{13}CO to be a variable in our least-squares refinement. In these calculations the reciprocal reduced mass of ^{13}CO appears as G_{11} in all molecules with an axial ^{13}CO, and as G_{nn} (n = 2 to 5) for different equatorial substitutions. The reduced masses for axial and equatorial groups were allowed to vary during the refinement, which now had seven variables (five force constants and two reduced masses). The results of the refinement are compared in Table VI columns *a* and *b* with those obtained using fixed reduced masses. Although the standard deviation 0.25 cm^{-1} was substantially reduced, almost to within experimental error, the maximum error was only slightly smaller, but on a different band. The most interesting point is that the ratios of the reciprocal reduced masses (axial 0.977 34, equatorial 0.977 37) were very close to Braterman's prediction (0.977 28).

(c) Effect of C–O/C–S Coupling. The C–S stretching band of the ^{13}CO enriched sample of $Cr(CO)_5CS$ was identical in line width and position to that of the unenriched compound. We therefore carried out calculations to see whether this implies that C–O/C–S vibrational coupling is absent in $Cr(CO)_5CS$. Three new force constants were introduced into the force field, k_{cs}, k_{cs-eq}, k_{cs-ax}. Initial values were guessed for these force constants and the whole CS/CO factored force field was refined as before. The absence of any ^{13}CO induced shift in ν_{C-S} or $C^{34}S$ satellites on ν_{C-O} made the refinement underdetermined and the values of the final force constants depended on the initial inputs. Table VI column *c* gives a typical example where initially $k_c = k_{c'} = 30$, $k_t = 60$, $k_{cs-eq} = 50$, and $k_{cs-ax} = 100\ N\ m^{-1}$. The final values still have k_{cs-ax} as the strongest interaction in the molecule, but nevertheless the frequency shift predicted for ν_{C-S} between $Cr(^{12}CO)_5CS$ and $Cr(^{13}CO)_5CS$ was only 0.08 cm^{-1}, which would not be experimentally detectable. Thus, although the frequencies of all the bands of $Cr(^{12}CO)_{5-x}(^{13}CO)_xCS$ can be fitted by neglecting CO/CS coupling, there is no evidence to show that such a coupling is not occurring.[29]

(d) Band Intensities. In the model[3,13,25] which successfully predicted the spectrum of ^{13}CO enriched $Cr(CO)_5CS$ (Figure 4b), the intensities of the C–O stretching bands of $Cr(CO)_5CS$ depend on the force constants, the bond angle, θ, and the ratio of the dipole moment derivatives, μ'_{ax}/μ'_{eq} (Figure 5b). $Cr(^{12}CO)_5CS$ has three C–O stretching bands ($2\ a_1$ + e), and since the force constants have already been fixed using band positions, the relative intensities of these bands allow θ and μ'_{ax}/μ'_{eq} to be calculated exactly. Using the equations of Braterman, Bau, and Kaesz,[25] and the observed intensity ratios R_1 ($I_{a_1,high}/I_{a_1,low}$) = 0.5 ± 0.05 and R_2 ($I_e/I_{a_1,low}$) = 3 ± 0.3, the values obtained are: $\theta = 82.8 \pm 1°$ ($122 \pm 1.8°$) and $\mu'_{ax}/\mu'_{eq} = 1.39 \pm 0.08$ (0.59 ± 0.04). The figures in parentheses are the out-of-phase solution which is obtained when $(R_1)^{1/2}/(R_2)^{1/2}$ is negative.

Although the crystallographic structure of $Cr(CO)_5CS$ is still awaited, both bond angles seem highly improbable for a pseudooctahedral $Cr(CO)_5CS$ molecule. The strange angle is not peculiar to $Cr(CO)_5CS$, nor is it the effect of matrix isolation, since the band intensities of $W(CO)_5CS$ in decalin solution give a similar angle. Using the intensity ratios reported by Angelici and Dombek,[26] $R_1 = 0.65$ and $R_2 = 5.4$, the calculated values are $\theta = 81.6$ (116°) and $\mu'_{ax}/\mu'_{eq} = 1.05$ (0.463). It has already been shown that the "in-phase" solution for $Cr(CO)_5$ reproduces the observed spectrum of $Cr(^{12}CO)_{5-n}(^{13}CO)_n$ much more closely than the out-of-phase solution, and the same was found in this case. Thus we have the somewhat paradoxical situation of an unrealistic bond angle, 83°, giving a very good simulation of the observed spectrum of $Cr(^{12}CO)_{5-n}(^{13}CO)_nCS$ (Figure 4b) while the chemically more realistic angle of 90° did not. For $\theta = 90°$ and $\mu'_{ax}/\mu'_{eq} = 1$ the intensity ratios calculated for $Cr(^{12}CO)_5CS$ are $R_1 = 0.22$ (obsd 0.5) $R_2 = 4.87$ (obsd 3).

This unrealistic bond angle is unexpected since a similar treatment gave the correct bond angle for $HMn(CO)_5$[25] and chemically resonable bond angles for matrix isolated $Cr(CO)_5$.[3] However, using ir band intensities, an incorrect bond angle is also calculated for η^5-$C_5H_5Mn(CO)_2CS$. In this molecule, the $M(CO)_2$ unit, C_s symmetry, has two C–O stretching modes (a′ + a″) and the angle between the two CO groups is related to the band intensities by the equation $\tan^2 \theta/2 = I_{a''}/I_{a'}$. Butler and Johansson have reported[27] the intensities of these bands, $I_{a''} = 15.4$ and $I_{a'} = 11.5$, which give a bond angle of 98.3°, substantially different from the observed value of 92°. The reason for the anomalous bond angles in both this compound and $Cr(CO)_5CS$ appears to lie in the neglect of the coupling of the *C–O, C–S, and M–C* vibrations and the π-acceptor properties of the CS group. A detailed analysis of this problem, which will be presented elsewhere,[28] suggests that the correct angles will be calculated for $M(CO)_nX$ species, where X is a vacant site or a ligand which is not a π acceptor. If, however, X is a diatomic ligand with a reduced mass comparable to CO (e.g., CS and N_2) and with significant vibrational coupling to the CO vibrations or a π-acceptor ligand, then the calculated bond angle will be incorrect. Nevertheless this incorrect bond angle will still reproduce the observed spectrum. Thus the "effective" bond angle can be imagined as arising from a neglect of coupling in intensity calculations analogous to that which gives rise to Braterman's "effective" reduced mass in wavenumber calculations.

C_{4v} $Cr(CO)_4CS$. As with $Cr(CO)_5CS$ the bands of the spectrum of C_{4v} $Cr(^{12}CO)_{4-n}(^{13}CO)_nCS$ were assigned using the Cotton–Kraihanzel approximation[23] $k_t = 2k_c$ (Figure 5c) and the frequencies of the bands of $Cr(^{12}CO)_4CS$, and the force constants were then refined. The matrix splittings of the bands were overcome, in general, by entering the mean wavenumber of the split components. This procedure has been justified previously for $Fe(CO)_4$,[12] where it was shown that it is the positions of the unsplit bands which are most important for determining the force constants. However, the bands are so split in this case that the fit is still rather poor. The origin of these splittings is discussed in greater detail in a subsequent paper.[6]

The splitting of the e mode made the relative intensities of the strong e mode and weak a_1 mode very difficult to estimate. Spectrum 4d is plotted with a bond angle of 96.5° (see Figure 5d) which corresponds to an intensity ratio $I_e/I_{a_1} \sim 80$ (cf. Figure 2).

C_s $Cr(CO)_4CS$. (a) Band Assignment. $Cr(^{12}CO)_4CS$ has four C–O stretching vibrations (3 a′ + a″) and seven force constants (Figure 5e). The most intense band, 1975.6 cm^{-1}, was provisionally assigned to the a″ mode. Since the remaining three bands all had the same symmetry (a′), the algebraic solution for the force approximate constants involved an unpleasant cubic equation and it was found simpler to use an iterative method. Two approximate force fields were used. Initially the approximation $k_2 = k_3$, $k_{12} = k_{13}$, $k_{33} = 2k_{23}$ was used but this failed to converge, if the band at 1975.6 cm^{-1} was assumed to have a″ symmetry. The second approximation, $k_{12} = k_{13} = k_{23} = {}^1/_2k_{33}$, converged to give an *exact* solution. Fortunately these approximate force constants allowed most of the bands to be assigned for the complete refinement. In this refinement the wavenumber of the stronger component of the a″ mode (Figure 2b) was used.

From the force constant refinement, there is no theoretical reason why the CS group should be trans to group 2 rather than group 1 (see Figure 5e). The position of the CS group was chosen by analogy with $Cr(CO)_5$ where the axial CO group has a force constant (Ar matrix, 1539.5 N m^{-1})[3], substantially less than that of the basal CO groups (1621.4 N m^{-1}). Thus in C_s $Cr(CO)_4CS$ (**3**) the CO group with the lowest force constant (1552.1 N m^{-1}) was assigned to the axial position and the groups with similar, higher force constants (1653.6 and 1635.2 N m^{-1}) were assigned to the basal positions.

(b) Bond Angles. Although the C_s isomer has three bond angles and two dipole moment derivative ratios (Figure 5f), $Cr(^{12}CO)_4CS$ has only four bands. This means that the calculation of bond angles is seriously underdetermined with three intensity ratios and five unknowns. The observed relative intensities were 2069.3 (0.36), 2011.3 (0.5), 1975.6 (1), and 1949.3 (0.54) with about 10% error in the measurements. Several solutions, which gave the correct intensity ratios, were found by trial and error. All predicted similar intensity patterns for the isotopically enriched molecules. The spectrum illustrated in Figure 4f used $\theta_1 = 90$, $\theta_2 = 90$, $\theta_3 = 194°$, $\mu'_1/\mu'_3 = 1.1$, and $\mu'_2/\mu'_3 = 1.3$, which gave relative intensities 2069.3 (0.38), 2011.3 (0.49), 1975.6 (1), and 1949.3 (0.49). Thus some of the differences between the observed and calculated spectra (Figures 4e and 4f) can be ascribed to these approximate parameters, but it was felt that, because of matrix splittings, the data did not justify a more rigorous refinement of the bond angles.

(c) Calculations for a C_{2v} Molecule. Two band assignments were used: 2069.3 (a_1), 2011.3 (b_1), 1975.6 (a_1), and 1949.3 (b_2); and 2069.3 (a_1) 2011.3 (a_1) 1975.6 (b_1), and 1949.3 (b_2). For both of these assignments approximate force constants were calculated using the approximation $k_{11} = k_{22}$ which has proved successful for $Fe(CO)_4$[12] and $Mo(CO)_4$.[4] From the force constants and the band intensities, bond angles and dipole moment derivative ratios were calculated and used to predict the spectrum of the ^{13}CO enriched molecules. At this stage the first assignment was rejected as it predicted that the 2011.3 cm^{-1} band should be three times as intense as the 1975.6 cm^{-1} band in the isotopic spectrum. Inspection of Figure 4e shows clearly that it is not. The approximate force constants, derived from the second assignment, were not refined further, and the values used to calculate spectrum g in Figure 4 were: $k_1 = 1639.8$, $k_2 = 1598.0$, $k_{11} = k_{22} = 63.077$, and $k_{12} = 21.509$ N m^{-1}. The bond angles were $\theta_1 = 195.8°$ and $\theta_2 = 77.3°$, and the dipole moment derivative ratio $\mu'_1/\mu'_2 = 1.168$ (see Figure 5g and 5h).

Registry No. $Cr(CO)_5CS$, 50358-90-2; $W(CO)_5CS$, 50358-92-4; $Cr(CO)_4CS$ isomer 2, 59752-96-4; $W(CO)_4CS$ isomer 2, 59752-97-5; $Cr(CO)_4CS$ isomer 3, 59780-38-0; $W(CO)_4CS$ isomer 3, 59780-39-1.

References and Notes

(1) J. J. Turner, *Angew Chem., Int. Ed. Engl.*, **14**, 304, (1975); J. K. Burdett and J. J. Turner, "Cryogenic Chemistry", G. A. Ozin and M. Moskovits,

Ed., Wiley-Interscience, New York, N.Y., to be published.

(2) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971).

(3) R. N. Perutz and J. J. Turner, *Inorg. Chem.*, **14**, 262 (1975).

(4) R. N. Perutz and J. J. Turner, *J. Am. Chem. Soc.*, **97**, 4791, 4800 (1975).

(5) R. J. Angelici and B. D. Dombek, *J. Am. Chem. Soc.*, **95**, 7516 (1973).

(6) M. Poliakoff, to be published.

(7) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1351 (1973).

(8) R. N. Perutz, Ph.D. Thesis, Cambridge University, 1974.

(9) E. P. Kündig and G. A. Ozin, *J. Am. Chem. Soc.*, **96**, 3820 (1974).

(10) J. K. Burdett, M. A. Graham, R. N. Perutz, M. Poliakoff, A. J. Rest, J. J. Turner, and R. F. Turner, *J. Am. Chem. Soc.*, **97**, 4804 (1975).

(11) H. Haas and R. K. Sheline, *J. Chem. Phys.*, **47**, 2996 (1967); J. H. Darling and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1079 (1973).

(12) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 2276 (1974).

(13) J. K. Burdett, H. Dubost, M. Poliakoff, and J. J. Turner, "Advances in Infra-red and Raman Spectroscopy", Vol. 2, R. J. Clark and R. Hester, Ed., Heyden, London, to be published.

(14) It should be noted that the relative values of the interaction force constants ($k_{c'} = 1.08k_c = 0.510k_t$) are very close to those assumed in the Cotton–Kraihanzel approximation[23] ($k_{c'} = k_c = 0.5k_t$). It is also interesting that the inactive b_2 mode of $Cr(^{12}CO)_5CS$ is predicted to be at 2024.9 cm^{-1}, only 0.6 cm^{-1} away from the observed a_1 band 2025.5 cm^{-1}, since these modes correlate with the two degenerate components of the e mode of a molecule with O_h symmetry, e.g., $Cr(CO)_6$.

(15) O. Crichton, M. Poliakoff, A. J. Rest, and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1321 (1973).

(16) J. K. Burdett, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J. Chem. Soc., Chem. Commun.*, 157 (1975).

(17) Under the C_{4v} point group, only a_1 and e symmetry transitions are dipole allowed. The transition responsible for the ~300 nm absorptions must originate from either a b_2 or e orbital giving four allowed transitions: $a_1 \leftarrow e$ (e), $b_2 \leftarrow e$ (e), $e \leftarrow b_2$ (e), and $e \leftarrow e$ (a_1 + e). Since the photochemically active transition behaves as if it had overall a_1 symmetry it must therefore be due to an $e \leftarrow e$ transition. The assignment of actual band symmetries is complicated because not only does this transition have mixed symmetry (a_1 + e) but also there is considerable band overlap (Figure 7).

(18) J. K. Burdett, R. N. Perutz, M. Poliakoff, and J. J. Turner, to be published.

(19) J. D. Black and P. S. Braterman, *J. Organomet. Chem.*, **63**, C19 (1973).

(20) M. Poliakoff, unpublished results.

(21) In previous studies[3,4,12] we have used gas phase photochemical exchange with ^{13}CO. In this case, gas phase photolysis not only caused enrichment but also rapidly generated $M(CO)_6$. The reaction may well have been the result of decomposition, followed by reaction of the metal with CO,

$$M(CO)_5CS \xrightarrow{h\nu} M(solid) \xrightarrow{CO} M(CO)_6$$

since a metal mirror was formed on the side of the Pyrex bulb during photolysis. On the other hand the solution photolysis produced no detectable increase in the amount of $Cr(CO)_6$ in the sample, and negligible ^{13}CO enrichment of the $Cr(CO)_6$.

(22) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Faraday Trans. 2*, **70**, 93 (1974).

(23) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(24) P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, London, 1975, pp 24–36.

(25) P. S. Braterman, R. Bau, and H. D. Kaesz, *Inorg. Chem.*, **6**, 2097 (1967).

(26) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, in press.

(27) I. S. Butler and D. A. Johansson, *Inorg. Chem.*, **14**, 701 (1975).

(28) J. K. Burdett, M. Poliakoff, and J. J. Turner, to be published.

(29) **Note Added in Proof.** A recent general quadratic valence force field calculation on these molecules (I. S. Butler, A. Garcia-Rodriguez, K. Plowman, and C. F. Shaw III, to be published) suggests that the CO/CS coupling is *indeed* comparable to the CO/CO coupling.

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Chemistry of Metal Carbonyl Anions. 6.[1] Preparation and Properties of Metallodithiocarboxylate Anions[2]

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Carbon disulfide reacts with highly nucleophilic carbonyl monoanions including (η^5-dienyl)$Fe(CO)_2^-$ (dienyl = C_5H_5, C_5H_4Me, C_5Me_5), $Mn(CO)_4P(C_5H_{11})_3^-$, and $Re(CO)_5^-$ to generate a new class of organometallic compounds which may be called metallodithiocarboxylate anions. Spectral and chemical properties of these thermally unstable anions are discussed including the synthesis of methyl- and triphenylstannyl derivatives which are believed to contain monodentate metallodithiocarboxylate groups. The synthesis of the first well-characterized species containing a bridging *monodentate* metallodithiocarboxylate group, $[C_5H_5Fe(CO)_2]_2CS_2$, is described. The latter is also the first example of a metal carbonyl complex in which a carbon disulfide unit is formally inserted into a metal–metal bond.

Introduction

The ability of transition metal fragments to mimic the properties of electronically equivalent main-group moieties[3] has been utilized recently in the preparation of a variety of interesting new classes of organometallic compounds, including metalloacetylacetonates in which a 15-electron transition metal fragment plays the role of a 5-electron carbyne function[4] and Fischer type carbene complexes where a 16-electron $M(CO)_5$ unit formally replaces a 6-electron oxygen atom in an organic ester.[5] In view of the close parallels in the chemistry of metal carbonyl monoanions (containing 17-electron neutral fragments) and classical pseudohalides[3] and observations that certain of the latter species, notably N_3^- and CN^-, form 1:1 adducts with carbon disulfide,[6] we expected that carbonyl monoanions would form analogous products, MCS_2^-, which may be called metallodithiocarboxylate anions. While this work was in progress,[2] two reports on related studies appeared. The first concerned the synthesis and structure of a platinum(II) complex containing a bidentate metallodithiocarboxylate group,[7] while the second dealt with the synthesis of coordinated trithiocarbonates from the interaction of carbon disulfide with metal carbonyl anions.[8] Previous to our work, only two reports on similar reactions have appeared in the literature. Wilkinson and co-workers synthesized a complex of stoichiometry $[(NC)_5CoSC(S)Co(CN)_5]^{6-}$, suggested to contain a unidentate metallodithiocarboxylate group, from the reaction of $Co(CN)_5^{3-}$ with CS_2.[9] However, another group formulated the same compound as $[(NC)_5CoS{=}C{=}SCo(CN)_5]^{6-}$, having a linear CS_2 unit.[10] Also, Busetto and Angelici reported that $C_5H_5Fe(CO)_2^-$ reacts with CS_2 to yield $C_5H_5Fe(CO)_2CS_2^-$ but presented no spectral or analytical proof for the existence of this anion.[11] This present study was undertaken in order to obtain spectral and chemical proof for the existence of metallodithiocarboxylate anions, to determine which factors promote the reaction of carbonyl anions with CS_2, and to investigate the possibility that these species might behave as organometallic analogues of dithiocarbamates, an extraordinarily versatile and important class of ligands.[6]

General Procedures and Materials

All operations were carried out under an atmosphere of purified nitrogen or argon, further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate, and